

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: May 15, 2008

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents

United States Patent and Trademark Office

P.O. Box 1450

Alexandria, VA 22313-1450

APPEAL BRIEF

PART IX

CFR 37 § 41.37(c) (1) (ix)

SECTION 1

VOLUME 5

Part 1

BRIEF ATTACHMENTS AA TO AL

Respectfully submitted,

/Daniel P Morris/

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BRIEF ATTACHMENT AA

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: March 1, 2005

Applicants: Bednorz et al.

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FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT AA

1989

Powder Diffraction File

Inorganic Phases

Alphabetical Index (Chemical and Mineral Name)



INTERNATIONAL CENTRE FOR DIFFRACTION DATA

Powder Diffraction File

Alphabetical Index Inorganic Phases 1989

Compiled by the JCPDS—International Centre for Diffraction Data in cooperation with the American Ceramic Society, American Crystallographic Association, American Society for Testing and Materials, Australian X-Ray Analytical Association, British Crystallographic Association, The Clay Minerals Society, Deutsche Mineralogische Gesellschaft, The Institute of Physics, The Mineralogical Association of Canada, The Mineralogical Society of America, Mineralogical Society of Great Britain and Ireland, National Association of Corrosion Engineers, and Société Française de Minéralogie et de Cristallographie.



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*formerly the
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BRIEF ATTACHMENT AB

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In re Patent Application of

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THIRD SUPPLEMENTAL AMENDMENT

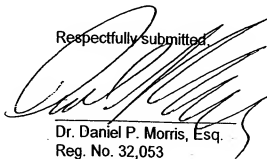
Sir:

In response to the Office Action dated July 28, 2004, please consider the following:

The attachments referred to herein A to Z and AA are in the FIRST SUPPLEMENTAL AMENDMENT. The Attachments AB to AG are attached herein.

Please charge any fee necessary to enter this paper and any previous paper to deposit account 09-0468.

Respectfully submitted,



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ATTACHMENT AB

Synthesis of cuprate superconductors*

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Abstract. There has been unprecedented activity pertaining to the synthesis and characterization of superconducting cuprates in the last few years. A variety of synthetic strategies has been employed to prepare pure monophasic cuprates of different families with good superconducting properties. Besides the traditional ceramic method, other methods such as coprecipitation and precursor methods, the sol-gel method, the alkali flux method and the combustion method have been employed for the synthesis of cuprates. Depending on the requirements, varying conditions such as high oxygen or hydrostatic pressure and low oxygen fugacity are employed in the synthesis. In this review, we discuss the synthesis of the various types of cuprate superconductors and point out the advantages and disadvantages of the different methods. We have provided the necessary preparative details, presenting the crucial information in tabular form wherever necessary.

1. Introduction

Since the discovery of high- T_c superconductivity in the La-Ba-Cu-O system [1], a variety of cuprate superconductors with T_c s going up to 128 K have been synthesized and characterized [2, 3]. No other class of materials has been worked on so widely and intensely in recent years as have the cuprate superconductors. Several methods of synthesis have been employed for preparing the cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Especially noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distances in the solid state [3, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed. In this review, we will discuss the preparation of cuprate superconductors by the different methods, mentioning

the special features of each method and the conditions employed for the synthesis. In table 1, we give a list of the cuprate superconductors discussed in this review along with their structural parameters and approximate T_c values. Preparative conditions such as reaction temperature, oxygen pressure, hydrostatic pressure and annealing conditions are specified in the discussion and given in tabular form where necessary. It is hoped that this review will be found useful by practitioners of the subject as well as those freshly embarking on the synthesis of these materials.

2. Ceramic method

The most common method of synthesizing inorganic solids is by the reaction of the component materials at elevated temperatures. If all the components are solids, the method is called the ceramic method [5]. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Platinum, silica or alumina containers are generally used for the synthesis of metal oxides. The starting materials are metal oxides, carbonates, or other salts, which are mixed, homogenized and heated at a given temperature sufficiently long for the reaction to be completed. A knowledge of the phase diagram is useful in fixing the composition and conditions in such a synthesis.

The ceramic method generally requires relatively high temperatures (up to 2300 K) which are generally attained by resistance heating. Electric arc and skull

* Contribution No 874 from the Solid State and Structural Chemistry Unit.

Table 1. Structural parameters and approximate T_c values of cuprate superconductors.

Cuprate	Structure	T_c (K) (max. value)
1 La_2CuO_4	Bmm; $a = 5.355$, $b = 5.401$, $c = 13.15$ Å	39
2 $\text{La}_{2-x}\text{Sr}_x(\text{Ba})_x\text{CuO}_4$	I4/mmm; $a = 3.779$, $c = 13.23$ Å	35
3 $\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.825$, $c = 19.42$ Å	60
4 $\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821$, $b = 3.885$, $c = 11.676$ Å	93
5 $\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84$, $b = 3.87$, $c = 27.24$ Å	80
6 $\text{Y}_2\text{Ba}_5\text{Cu}_7\text{O}_{15}$	Ammm; $a = 3.851$, $b = 3.869$, $c = 50.29$ Å	93
7 $\text{Bi}_2\text{Sr}_2\text{CuO}_8$	Amaa; $a = 5.362$, $b = 5.374$, $c = 24.822$ Å	10
8 $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	A2aa; $a = 5.409$, $b = 5.420$, $c = 30.93$ Å	92
9 $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_{10}$	A2aa; $a \sim 5.39$, $b \sim 5.40$, $c \sim 37$ Å	110
10 $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888$, $c = 17.28$ Å	25
11 $\text{Tl}_2\text{Ba}_2\text{CuO}_8$	A2aa; $a = 5.468$, $b = 5.472$, $c = 23.238$ Å; I4/mmm; $a = 3.866$, $c = 23.239$ Å	92
12 $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855$, $c = 29.318$ Å	119
13 $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{O}_{10}$	I4/mmm; $a = 3.85$, $c = 35.9$ Å	128
14 $\text{Ti}(\text{BaLa})\text{CuO}_8$	P4/mmm; $a = 3.83$, $c = 9.55$ Å	40
15 $\text{Ti}(\text{SrLa})\text{CuO}_8$	P4/mmm; $a \sim 3.7$, $c \sim 9$ Å	40
16 $(\text{Ti}_{0.8}\text{Pb}_{0.2})\text{Sr}_2\text{CuO}_8$	P4/mmm; $a = 3.738$, $c = 9.01$ Å	40
17 $\text{TiCaBa}_2\text{Cu}_2\text{O}_8$	P4/mmm; $a = 3.856$, $c = 12.754$ Å	103
18 $(\text{Ti}_{0.8}\text{Pb}_{0.2})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$, $c = 12.05$ Å	90
19 $\text{TiSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$, $c = 12.10$ Å	80
20 $\text{TiCa}_2\text{Ba}_2\text{Cu}_2\text{O}_8$	P4/mmm; $a = 3.853$, $c = 15.913$ Å	110
21 $(\text{Ti}_{0.8}\text{Pb}_{0.2})\text{Sr}_2\text{Ce}_2\text{Cu}_2\text{O}_8$	P4/mmm; $a = 3.81$, $c = 15.23$ Å	120
22 $\text{TiBa}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_8$	I4/mmm; $a \sim 3.8$, $c \sim 29.5$ Å	40
23 $\text{Pb}_2\text{Sr}_2\text{Ln}_{0.5}\text{Ce}_{0.5}\text{Cu}_2\text{O}_8$	Cmmm; $a = 5.435$, $b = 5.463$, $c = 15.817$ Å	70
24 $\text{Pb}_2(\text{Sr}, \text{La})_2\text{Cu}_2\text{O}_8$	P2 ₂ ; $a = 5.333$, $b = 5.421$, $c = 12.609$ Å	32
25 $(\text{Pb}, \text{Cu})\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820$, $c = 11.826$ Å	50
26 $(\text{Pb}, \text{Cu})\text{Sr}_2(\text{Eu}, \text{Eu}, \text{Ca})\text{Cu}_2\text{O}_7$	I4/mmm; $a = 3.837$, $c = 29.01$ Å	25
27 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95$, $c = 12.07$ Å	30
28 $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902$, $c = 3.35$ Å	110
29 $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942$, $c = 3.393$ Å	40

techniques give temperatures up to 3300 K while high-power CO_2 lasers give temperatures up to 4300 K. The main disadvantages of the ceramic method are the following:

(i) The starting mixtures are inhomogeneous at the atomic level.

(ii) When no melt is formed during the reaction, the entire reaction has to occur in the solid state, first by a phase boundary reaction at the points of contact between the components and later by the diffusion of the constituents through the product phase. With the progress of the reaction, diffusion paths become longer and the reaction rate slower; the reaction can be speeded up to some extent by intermittent grinding between heating cycles.

(iii) There is no simple way of monitoring the progress of the reaction. It is by trial and error that one decides on the appropriate conditions required for the completion of the reaction. Because of this difficulty, with the ceramic method one often ends up with mixtures of reactants and products. Separation of the desired products from such mixtures is difficult, if not impossible.

(iv) Frequently it becomes difficult to obtain a compositionally homogeneous product even where the reaction proceeds nearly to completion.

Despite the above limitations, the ceramic method is widely used for the synthesis of a large variety of inorganic solids. In the case of the cuprate superconductors,

the ceramic method involves mixing and grinding the component oxides, carbonates or other salts, and heating the mixture, generally in pellet form, at the desired temperature. A common variation of the method is to heat a mixture of nitrates obtained by digesting the metal oxides/carbonates in concentrated HNO_3 and evaporating the solution to dryness. Heating is carried out in air or in an appropriate atmosphere, controlling the partial pressure of oxygen when necessary. In the case of thallium cuprates, because of the volatility and poisonous nature of the thallium oxide vapour, reactions are carried out in sealed tubes. In some of the earlier preparations, the thallium cuprates were synthesized in open furnaces. This is however, not recommended. A successful synthesis by the ceramic method depends on several factors which include the nature of the starting materials (the choice of oxides, carbonates), the homogeneity of the mixture of powders, the rate of heating as well as the reaction temperature and duration.

2.1. La_2CuO_4 -related 214 cuprates

Synthesis of alkaline-earth-doped $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Ca}, \text{Sr}$ and Ba) of K_2NiF_4 structure with superconducting transition temperatures up to 35 K is readily achieved by the ceramic method. Typically, the synthesis is carried out by reacting stoichiometric quantities of the oxides and/or carbonates around 1300 K in

oxygen atmosphere at 973 K after the starting [10]. Metal nitrates have also been used as starting materials for the synthesis [11-13]. By starting with metal nitrates, one obtains a more homogeneous starting mixture, since the hydrated metal nitrates have low melting points leading to a uniform melt in the initial stage of the reaction. Furthermore, nitrates provide an oxidative atmosphere, which is required to obtain the necessary oxygen content.

Stoichiometric La_2CuO_4 is an antiferromagnetic insulator. La_2CuO_4 prepared under high oxygen pressures, however, shows superconductivity ($T_c \sim 35$ K) since the oxygen excess introduces holes just as the alkaline earth dopants [14-16]. $\text{La}_2\text{CuO}_{4+\delta}$ (δ up to 0.05) has been synthesized by annealing La_2CuO_4 under an oxygen pressure of 3 kbar at 870 K [14, 15] or 23 kbar at 1070 K [16]. Oxygen plasma has also been used to increase the oxygen content.

The next homologue of La_2CuO_4 containing two Cu-O layers, $\text{La}_{1.6}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_8$ ($T_c \sim 60$ K), has been synthesized by using high oxygen pressures [17]. The synthesis involves heating the sample at an oxygen pressure of around 20 bar at 1240 K. The material prepared at ambient oxygen pressures (in air) is an insulator. Several other high-oxygen-pressure preparations have been reported on the $n=2$ member of the $\text{La}_{1-x}\text{Cu}_{2+x}\text{O}_{2n+1}$ homologous series by making use of commercially available high-pressure furnaces [18, 19]. In table 2, we have summarized the preparative conditions for 214 and related cuprate superconductors.

2.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other 123 cuprates

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with the orthorhombic structure can be easily prepared by the ceramic method. Most of the investigations of the 123 compound, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, have been carried out on the materials prepared by reacting Y_2O_3 and CuO with BaCO_3 [20, 21]. It is noteworthy that Rao *et al* [21] obtained monophasic $\text{YBa}_2\text{Cu}_3\text{O}_7$, as the $x = 1.0$ member of the $\text{Y}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_{7-x}$ series. In the method employed for preparing $\text{YBa}_2\text{Cu}_3\text{O}_7$, stoichiometric quantities of high-purity Y_2O_3 , BaCO_3 and CuO are ground thoroughly and heated initially in powder form around 1223 K for a period of 24 h. Following the calcination step, the powder is ground, pelletized and sintered at the same temperature for another 24 h. Finally, annealing is carried out in an atmosphere of oxygen around 773 K for 24 h to obtain the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase showing 90 K superconductivity. Oxygen annealing has to be carried out below the orthorhombic tetragonal transition temperature (~ 960 K); tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($0.6 \leq x \leq 1.0$) is not superconducting. Intermittent grinding is necessary to obtain monophasic, homogeneous powders. This kind of complex heating schedule often gives rise to microscopic compositional inhomogeneities. Furthermore, CO_2 released from the decomposition of BaCO_3 can react with $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ to form non-superconducting

the evolution of Cu_2O [22]. Some of the impurities or side products in the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ are BaCuO_2 , Y_2BaCuO_5 and $\text{Y}_2\text{Cu}_2\text{O}_5$ [24]. The ternary phase diagram given in figure 1 illustrates the complexities of this cuprate system.

Using BaO_2 as the starting material has two advantages. It has a lower decomposition temperature than BaCO_3 and the 123 compound is therefore formed at relatively low temperatures. BaO_2 acts as an internal oxygen source and the duration of annealing in an oxygen atmosphere is reduced to a considerable extent. Sharp superconducting transitions are observed in samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ made using BaO_2 . Slight excess of copper in the ceramic method is reported to give cuprates with sharper transitions [25]. Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is accomplished in a shorter period if one employs metal nitrates as the starting materials [13, 23]. In table 2, we present the conditions employed for preparing 123 cuprates by the ceramic method.

Other rare-earth cuprates of the 123 type, $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$, where $\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho, Er}$ and Tm (all with T_c values around 90 K) have also been prepared by the ceramic method [26, 27]. Oxygen annealing of these cuprates should also be carried out below the orthorhombic-tetragonal transition temperature [3]: La, 754 K; Nd, 837 K; Gd, 915 K; Er, 973 K; Yb, 976 K etc. Nearly 30% of Y can be substituted by Ca in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, retaining the basic crystal structure [28]; the T_c decreases with the increase in calcium content. Both La and Sr can be substituted at the Ba site in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [29-31]. With La, monophasic products are obtained for $0 \leq x \leq 1.0$ in $\text{YBa}_{1-x}\text{La}_x\text{Cu}_3\text{O}_{7-x}$, the T_c decreasing with increase in x . In the case of Sr substitution, monophasic products are obtained for $0 \leq x \leq 1.25$ in $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-x}$; high T_c is retained up to $x = 1.0$. Ceramic methods have also been used to prepare $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-x}$ solid solutions, where M generally stands for a transition element of the first series. In most

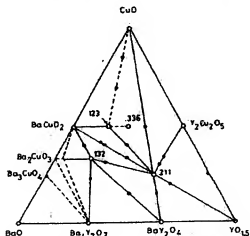


Figure 1. Phase diagram of the Y_2O_3 -BaO-CuO system at 1220 K (from [24]).

Table 2. Preparative conditions for the synthesis of 214, 123, 124 and 247 type cuprates by the ceramic method.

Compound	Starting materials	Preparative conditions			Comments	T_c (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{La}_2\text{CuO}_{4-x}$	$\text{La}_2\text{O}_3, \text{CuO}$	1273 873	24 h 12-48 h	O_2 O_2	3 kbar pressure	35 40	[15] [10]
$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_y)\text{CuO}_4$	$\text{La}_2\text{O}_3, \text{Sr}/\text{BaCO}_3, \text{CuO}$	1583	36 h	O_2			
	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}, \text{Sr}/\text{Ba}(\text{NO}_3)_2$	1273	20 h	air			
	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	873	18 h	O_2			
$\text{La}_{1-x}\text{Sr}_x\text{CaCu}_2\text{O}_8$	$\text{La}_2\text{CO}_7, \text{Yb}_2\text{O}_3, \text{Sr}(\text{NO}_3)_2$	1173	3 d	O_2		32	[13]
	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}, \text{CuO}$	1168	3 d	O_2			
		1153	2 d	O_2			
		1223	1 d	O_2			
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ *	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1773	1 d	O_2	20 atm	60	[17]
	$\text{Y}_2\text{O}_3, \text{BaO}_2, \text{CuO}$	1198	2 d	air		88	[20]
	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}, \text{Ba}(\text{NO}_3)_2$	1173	1 d	air		86	[22]
	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	1223	1 h	O_2		90	[13]
$\text{YBa}_2\text{Cu}_3\text{O}_{6-x}$ *	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1313	—	O_2	400 bar	81	[34]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$	1023	1 d	O_2	124 major phase + BaCuO_2 impurity	77	[35]
	volumes of Na_2CO_3 or K_2CO_3	1073	3 d	O_2	124 major phase + BaCuO_2 impurity	78	[36, 38]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$ or Na_2CO_3	1073	1 d	air	$\text{BaCuO}_2 + \text{Y}_2\text{BaCuO}_5$	78	[36]
	CuO or BaCO_3	1088	2 d	O_2	$\text{BaCuO}_2 + \text{Y}_2\text{BaCuO}_5$	79	[40]
	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$ + 0.2M NaNO_3 + 10 drops of dilute HNO_3	1088	10 d	O_2	124 single phase	75	[38]
	$\text{YBa}_2\text{Cu}_3\text{O}_7, \text{CuO}$	1083	3 d	O_2	124 major phase + BaCuO_2	90	[50]
$\text{Y}_{1-x}\text{Ba}_x\text{Cu}_3\text{O}_{7-x}$ *	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1203	8 h	O_2	19 bar	90	[50]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$	1153	5 d	O_2	Single phase	90	[38]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$ + 0.2M NaNO_3	1153	4 d	O_2	Single phase	90	[38]

* Other rare-earth derivatives of the type $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ are also prepared by this method. Oxygen annealing is carried out below the orthorhombic-tetragonal transition temperature [36, 37].

Other rare-earth derivatives of the type $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ are obtained by a similar procedure [38, 40].

* Other rare-earth derivatives of the type $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ are prepared by a similar procedure [38, 39].

2.3. $\text{YBa}_2\text{Cu}_3\text{O}_8$ (124), $\text{Y}_2\text{Ba}_2\text{Cu}_7\text{O}_{15}$ (247) and related cuprates

The first bulk synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_8$ was reported by Karpinski *et al* [34] who heated the mixture of oxides at 1313 K, under an oxygen pressure of 400 bar. Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_8$ by the conventional ceramic method without the use of high oxygen pressure suffered from some limitations due to kinetic factors. Cava *et al* [35] found that additives such as alkali carbonates enhance the reaction rate. The procedure involves two steps. In the first step Y_2O_3 , $\text{Ba}(\text{NO}_3)_2$ and CuO are mixed in the stoichiometric ratio and heated at 1023 K for 16–24 h in an oxygen atmosphere. In the second step, the pre-reacted powder is ground with an approximately equal volume of either Na_2CO_3 or K_2CO_3 powder and pellets of the resulting mixture are heated at 1073 K in flowing oxygen for 3 days. After the reaction, the product is washed with water to remove the excess alkali carbonate and dried by gentle heating in air. The product after this step has $\text{YBa}_2\text{Cu}_3\text{O}_8$ as the majority phase (T_c , 77 K) with little BaCuO_2 impurity. Other reaction rate enhancers such as NaNO_3 , KNO_3 , dilute HNO_3 and Na_2O_2 have also been used successfully (in small quantities) to prepare $\text{YBa}_2\text{Cu}_3\text{O}_8$ [36–38]. The 124 cuprate can also be prepared without the addition of a rate enhancer by the solid state reaction of Y_2O_3 , BaCuO_2 and CuO at 1088 K in flowing oxygen [36]. Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_8$ from the solid state reaction between $\text{YBa}_2\text{Cu}_3\text{O}_7$ and CuO in flowing oxygen has also been reported [39]. The synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_8$ by the ceramic method generally takes a long time and requires repeated grinding and pelletizing.

Other rare-earth 124 cuprates, $\text{LnBa}_2\text{Cu}_3\text{O}_8$ with $\text{Ln} = \text{Eu, Gd, Dy, Ho}$ and Er have been prepared by the ceramic method under an oxygen pressure of 1 atm [36, 40]. The T_c of these cuprates decreases with the increasing ionic radius of the rare earth. Calcium can be substituted at the Y site up to 10% in $\text{YBa}_2\text{Cu}_3\text{O}_8$, and the T_c increases from 79 K to 87 K in such substituted $\text{YBa}_2\text{Cu}_3\text{O}_8$ [41]. Lanthanum can be substituted for barium in $\text{YBa}_2\text{Cu}_3\text{O}_8$ [42]. Single phases of $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_8$ have been obtained for $0 \leq x \leq 0.4$ with the T_c decreasing with increase in x .

Extensive studies have been carried out on the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_8$ under high oxygen pressures [43, 44]. The P - T phase diagram of 124, 123 and 247 cuprates is shown in figure 2. High-oxygen pressure synthesis essentially involves the solid state reaction followed by sintering under high oxygen pressures. The typical sintering temperature and the pressure at which synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_8$ has been carried out are 1200 K and 120 atm of oxygen (for 8 h). By the use of high oxygen pressures [45], it is possible to prepare 124 compounds with other rare earths such as Nd and Sm , which is otherwise not possible under ambient pressures.

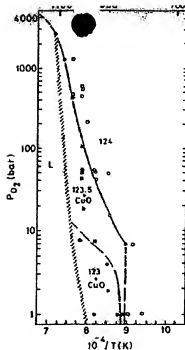


Figure 2. Phase diagram of the 124, 247 and 123 cuprates (from [43]).

A variety of substitutions has been carried out at the Y, Ba and Cu sites in $\text{YBa}_2\text{Cu}_3\text{O}_8$ under high oxygen pressures. Yttrium can be substituted up to 10% by Ca in $\text{YBa}_2\text{Cu}_3\text{O}_8$ giving a T_c of ~90 K [46]; 20% Ba has been substituted by Sr without affecting the T_c [47]. Single-phase iron-substituted $\text{YBa}_2\text{Cu}_{1-x}\text{Fe}_x\text{O}_8$ ($0 \leq x \leq 0.05$) has been prepared at an oxygen pressure of 200 bar [48]; the T_c falls monotonically with increasing iron concentration.

Bordet *et al* [49] first reported the preparation of $\text{Y}_2\text{Ba}_2\text{Cu}_7\text{O}_{15}$ under oxygen pressures of 100–200 bar. It was soon realized that $\text{Y}_2\text{Ba}_2\text{Cu}_7\text{O}_{15}$ can be synthesized by the ceramic method under an oxygen pressure of 1 atm by a procedure similar to that employed for $\text{YBa}_2\text{Cu}_3\text{O}_8$, except for the difference in the sintering temperature [36]. There is a narrow stability region between 1123 K and 1143 K for the 247 cuprate to be synthesized under 1 atm oxygen pressure. The best sintering temperature at which the 247 cuprate is formed is 1133 K. Other rare-earth 247 cuprates, $\text{Ln}_2\text{Ba}_2\text{Cu}_7\text{O}_{15}$ ($\text{Ln} = \text{Dy, Er}$), can also be prepared by this method [36, 38]. About 5% of Y can be replaced by Ca in $\text{Y}_2\text{Ba}_2\text{Cu}_7\text{O}_{15}$, and the T_c increases to 94 K [42]. Substitution of La at the Ba site is limited to ~10% in $\text{Y}_2\text{Ba}_2\text{Cu}_7\text{O}_{15}$, where the T_c decreases continuously with increasing lanthanum content [42].

Synthesis of 247 cuprates by the high-pressure oxygen method is generally carried out at 1203 K at an oxygen pressure of around 19 bar (for 8 h). This step is followed by slow cooling (typically 5°C min^{-1}) to room temperature at the same pressure [50]. Other rare-earth 247 compounds, $\text{Ln}_2\text{Ba}_2\text{Cu}_7\text{O}_{15}$ ($\text{Ln} = \text{Eu, Gd, Dy, Ho}$

and Er), have been prepared in the oxygen pressure range of 14–35 bar [50]. Preparative conditions for the 124 and 247 cuprates are given in table 2.

2.4. Bismuth cuprates

Although the ceramic method is widely employed for the synthesis of superconducting bismuth cuprates of the type $\text{Bi}_2(\text{Ca}, \text{Sr})_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$, it is generally difficult to obtain monophasic compositions, due to various factors [51, 52]. Both thermodynamic and kinetic factors are clearly involved in determining the ease of formation as well as phase purity of these cuprates. The $n=1$ member (2201) of the formula $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ appears to be stable around 1083 K and the $n=2$ member, $\text{Bi}_2(\text{Ca}, \text{Sr})_2\text{Cu}_2\text{O}_8$ (2122) around 1113 K. The $n=3$ member, $\text{Bi}_2(\text{Ca}, \text{Sr})_4\text{Cu}_3\text{O}_{10}$ (2223), can be obtained close to the melting point (1123 K) after heating for several days or even weeks. Of all the members of the $\text{Bi}_2(\text{Ca}, \text{Sr})_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$ family, the $n=2$ member (2122) seems to be most stable. Bi_2O_3 , which is often used as one of the starting materials, melts at around 1103 K. Increasing the reaction temperature therefore leads to preferential loss of volatile Bi_2O_3 . This results in micro-inhomogeneities and the presence of the unreacted oxides in the final product. Since these materials contain so many cations, partial reaction between various pairs of oxides leading to the formation of impurity phases in the final product cannot easily be avoided. A noteworthy structural feature of all these bismuth cuprates is the presence of superlattice modulation; the modulation has nothing to do with superconductivity.

Most of the above problems have been overcome by employing the matrix reaction method [53, 54]. This method reduces the number of reacting components and gives better products. In this method, synthesis is carried out by reacting the oxide matrix made from CaCO_3 , SrCO_3 and CuO with Bi_2O_3 in the temperature range of 1083–1123 K in air for a minimum period of 48 h. Quenching the samples in air from the sintering temperature or heating in a nitrogen atmosphere improves the superconducting properties of bismuth cuprates. The matrix reaction method yields monophasic $n=2$ (2122) and $n=3$ (2223) compositions showing T_c values of 85 K and 110 K respectively [55, 56]. Partial melting for a short period (~5 min) also favours the rapid formation of the $n=2$ (2122) and the $n=3$ (2223) members.

The $n=1$ member, $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, showing T_c in the range 7–22 K is a rather complicated system and has two structurally different phases near the stoichiometric composition [51, 57–60]. Many workers have varied the Bi/Sr ratio and obtained single-phase materials with a T_c of 10 K at a composition which is strontium deficient, $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_6$ [60, 61]. This cuprate is best prepared by reacting the oxides and/or carbonates of the constituent metals at 1123 K in air for extended periods of time. In figure 3 we show the phase diagram of the Bi–Sr–Cu–O system. The phase diagram of the

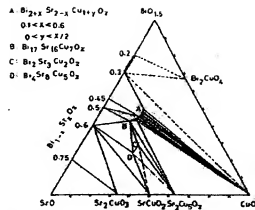


Figure 3. Phase diagram of the Bi–Sr–Cu–O system at 1110 K in air (from [60]).

Bi_2O_3 – SrO – CaO – CuO system at a constant Cu content is shown in figure 4.

Substitution of a small amount of lead for bismuth results in good superconducting samples of $n=2$ (2122) and $n=3$ (2223) members. A number of workers have therefore preferred to synthesize both $n=2$ (2122) and $n=3$ (2223) members with substitution of lead up to 25% in place of bismuth [58, 63–66]. They are obtained either by direct reaction of oxides and/or carbonates the cations or by the matrix reaction method.

Other than the matrix reaction method, melt quenching (glass route) [67, 68] and a semi-wet method [6] have been employed for the synthesis of superconducting bismuth cuprates. In the melt quenching method the mixture of starting materials (in the form of oxide and/or carbonates) is melted in a platinum or alumina crucible around 1473 K for a short period in air and then quenched in liquid nitrogen. The quenched specimens are given an annealing treatment around 1103 K in air to obtain the superconducting crystalline cuprates. This method has been shown to produce both $n=2$ (2122) and lead-doped $n=3$ (2223) members.

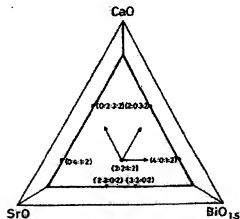


Figure 4. Section through the phase diagram of the Bi_2O_3 – SrO – CaO – CuO system at a constant CuO content of 28.6 mol% (from [62]).

semi-wet method involves the reaction between two precursors which precipitate separately. For example, in the preparation of $\text{Bi}_{1-x}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{10}$, a precipitate of Pb, Sr and Ca (as carbonates) and one of Bi and Cu (as oxalates) are reacted at 1138 K in air for a minimum period of 72 h. The duration of the reaction for the formation of 2223 phase is drastically reduced by this method.

The starting composition of the reactant materials plays an important role in the synthesis of these cuprates. For example, strontium deficiency in the $n = 1$ (2201) member favours monophasic compositions [59, 61]. Strontium deficiency also helps in obtaining a phase-pure $n = 2$ (2122) member [70]. Starting with a 4:3:3:4 stoichiometry of Bi:Ca:Sr:Cu, it has been possible to obtain a monophasic 2122 member [54, 71]. The $n = 3$ (2223) phase, on the other hand, is either obtained through the substitution of Bi by Pb (up to 25%) or by taking an excess of Ca and/or Cu [63-66, 72]. The problem of balancing between phase purity and high T_c of the cuprate gives rise to some difficulty in the synthesis of these cuprates. The coexistence of some of the members of the homologous series, especially in the form of polytypic intergrowths of different layered sequences, is also a problem. This problem is also encountered with thallium cuprates [73, 74].

The $n = 4$ phase, $\text{Bi}_{1-x}\text{Pb}_{0.5}\text{Ca}_3\text{Sr}_2\text{Cu}_2\text{O}_{12}$, which was observed in an electron micrograph along with $n = 3$ phase as an intergrowth, was synthesized in bulk by Rao *et al* [75] (with a small proportion of the $n = 3$ phase) by the ceramic method. The $n = 4$ phase has a slightly lower T_c (103 K), than the $n = 3$ phase. This cuprate has also been prepared by Losch *et al* [75].

A variety of substitutions has been carried out in superconducting bismuth cuprates employing the ceramic method [58, 76-79]; some of them are noteworthy. For example, the simultaneous substitution of Bi by Pb and Sr by La in $\text{Bi}_2\text{Sr}_2\text{CuO}_4$ results in a modulation-free superconductor of the formula $\text{BiPbSr}_{1-x}\text{La}_x\text{CuO}_4$ with T_c increased to 24 K [77]. Similarly, co-substitution of Bi by Pb and Ca by Y in the $n = 2$ member (2122) gives a modulation-free superconductor, $\text{BiPbY}_{0.5}\text{Ca}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_8$ with a T_c of 85 K [77]. Rare-earth substitution for Ca in $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ causes the T_c to go up to 100 K without the introduction of the $n = 3$ phase [58, 78]. As mentioned earlier, the $n = 3$ phase is stabilized by the partial substitution of lead in place of bismuth [63-65]. Another significant discovery is the iodine intercalation of the Bi-2122 superconductor [80]. Intercalation does not greatly affect the superconducting properties of the material; clearly, superconductivity is confined to the two-dimensional CuO_2 sheets in these materials.

Synthesis of a new series of superconducting cuprates of the general formula $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$ (Bi-2222 phase with $\text{Ln} = \text{Sm, Eu, Gd}$) containing a fluorite-like $(\text{Ln}_{1-x}\text{Ce}_x)_2\text{O}_2$ layer between the two CuO_2 sheets has been possible by the ceramic method [81]. Partial substitution of bismuth by lead increases

as at an air of O_2 with other rare earths

As mentioned earlier, one does not start with an exact stoichiometric composition to obtain the desired final product in the case of superconducting bismuth cuprates. Although structural studies (see for example [84]) indicate the presence of bismuth atoms over strontium and calcium sites as well, it is not possible to prescribe an exact initial composition to obtain the desired final stoichiometry. For example, starting from a nominal composition of $(\text{Bi}_{0.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_8)_x$, one ends up with the formation of the $n = 3$ (2223) member [65]. Therefore, for the purpose of characterizing the various members of the superconducting bismuth cuprates, one starts with some arbitrary composition and varies the synthetic conditions suitably to obtain the desired final product in pure form. The actual compositions of the final cuprate are quite unexpected (e.g. $\text{Bi}_{1.83}\text{Pb}_{0.30}\text{Sr}_{2.04}\text{Ca}_{1.68}\text{Cu}_2\text{O}_8$) as found from analytical electron microscopy [85]. In table 3 we have summarized the preparative conditions of all the members of $\text{Bi}_2(\text{Ca, Sr})_{x+1}\text{Cu}_2\text{O}_{2x+4}$ family.

2.5. Thallium cuprates

The conventional ceramic method employed for the synthesis of 214, 123 and bismuth cuprates has to be modified in the case of thallium cuprates of the $\text{Tl}_2\text{Ca}_{x-1}\text{Ba}_2\text{Cu}_2\text{O}_{2x+4}$, $\text{TlCa}_{x-1}\text{Ba}_2\text{Cu}_2\text{O}_{2x+3}$ and $\text{TlCa}_{x-1}\text{Sr}_2\text{Cu}_2\text{O}_{2x+3}$ families due to the toxicity and volatility of thallium oxide. In the early days, the reaction was carried out in an open furnace in air or oxygen atmosphere at high temperatures (1150-1180 K) for 5-10 min [86, 87]. In a typical procedure, the mixture of reactants in the form of a pellet was quickly introduced into the furnace maintained at the desired temperature. Since melt-solid reactions take place faster than solid-solid reactions, the product was formed quickly by this method [87]. Although this method requires a very short duration of heating, it results in the loss of thallium, leading to the danger of inhaling thallium oxide vapour. Some workers have taken certain precautions not to release the Tl_2O_3 vapour into the open laboratory, but the method is still not recommended. Furthermore, the formation of the desired phase is not ensured under the open reaction conditions. Synthesis of thallium cuprates has therefore been carried out in closed containers (sealed tubes) by most workers. By this method, both polycrystalline samples and single crystals can be prepared, since the reaction is carried out over longer periods. Better control of stoichiometry, homogeneity of phases and the total avoidance of the inhalation of toxic thallium oxide vapours are some of the advantages of carrying out sealed tube reactions.

Closed reaction conditions have been achieved in different ways. The reactant mixture is sealed in gold [88] or silver tubes [89] or in a platinum [90] or nickel

Table 3. Preparative conditions for the synthesis of bismuth cuprates by the ceramic method.

Starting composition	Conditions*		Product	T_s (K)	Ref.
	Temp. (K)	Time			
$\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1103	2 d	2201 major phase	20	[61]
$\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1123	1 d	2201 major phase	9	[57]
$\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_x$	1123	2 d	Single phase	10	[59, 61]
$\text{BiPbSr}_{1-x}\text{La}_x\text{CuO}_x$	1150	1 d	Single phase	24	[77]
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_x$	1103	5 d	Single phase	65	[91]
$\text{Bi}_2\text{Ca}_{1-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_x$	1103	3 d	2122 major phase	60	[65]
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1108	2 d	2122 single phase	85	[71]
$\text{Bi}_2\text{Sr}_{1-x}\text{CaCu}_2\text{O}_x$	1113	3 d	2122 single phase	85	[70]
$\text{BiPbSr}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_x$	1200	1 d	2122 single phase	85	[77]
$\text{Bi}_2\text{Pb}_{0.4}\text{Ca}_{0.6}\text{Sr}_{1.6}\text{Cu}_2\text{O}_x$	1140	5 d	2223 major phase	120	[56]
$\text{Bi}_{1-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1100	4 d	2223 major phase	105	[64]
$\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_x$	1153	10 d	2223 single phase	110	[72]
$\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_2\text{O}_x$	1153	5 d	2223 major phase	105	[65]
$\text{BiCaSrCu}_2\text{O}_x$	1143	5 d	2223 major phase	120	[65]
$\text{Bi}_{1-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1133	5 d	2223 major phase	108	[64]
$\text{Bi}_2\text{Gd}_{1-x}\text{Ce}_x\text{Sr}_2\text{Cu}_2\text{O}_x$	1273	10 h	2222 single phase	30	[81]

* All the preparations carried out in air.

* Obtained by matrix reaction method.

alloy (Inconel) container [91] closed tightly with a silver lid. Alternatively, the reactant mixture is taken in the form of a pellet, wrapped in a platinum [92] or gold [93] foil and then sealed in a quartz tube. This method has the advantage of carrying out the reaction under a vacuum. Some workers place the reactant pellet in an alumina crucible [94] which is then sealed in a quartz ampoule. Thallium-excess starting compositions have been employed by a few workers to compensate for the thallium loss during the reaction [95].

In the preparation of the thallium cuprates, the matrix reaction method is often employed. Here, a mixed oxide containing all the metal ions other than the volatile thallium oxide is first prepared by reacting the corresponding oxides and/or carbonates around 1200 K for 24 h in air [89, 96]. The freshly prepared mixed oxide is then taken with a calculated quantity of Tl_2O_3 and heated at appropriate temperatures in a sealed tube. This method is desirable when a carbonate is used as the starting material. Some of the thallium cuprates have been prepared by a modified matrix method [97] wherein a thallium-containing precursor such as $\text{Ba}_2\text{Tl}_2\text{O}_5$ is prepared first and then reacted with other components under closed conditions. Thallium-containing precursors are less volatile than Tl_2O_3 , so that the loss of thallium is minimized during the preparation.

Thermodynamic and kinetic factors associated with the synthesis of thallium cuprates are complex due to the existence of various phases which are structurally related and which can therefore intergrow with one another. In fact, one of the common defects that occurs in the thallium cuprates is the presence of random intergrowths between the various layered phases [98]. Furthermore, many of the thallium, lead and bismuth superconductors are metastable phases which are entropy stabilized [99]. The temperature of the reac-

tion, the sintering time and the starting composition are therefore all crucial to obtaining monophasic products (table 4).

The effect of the starting composition is best illustrated by the formation of the $n=3$ phase of the bilayer thallium cuprates ($\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{O}_{10}$). Synthesis of this compound starting from the stoichiometric mixture of the oxides corresponding to the ideal composition often yields the $n=2$ member of the family. It was found that starting with compositions rich in Ca and/or Cu (namely $\text{TlCa}_3\text{BaCu}_2\text{O}_x$, $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{O}_x$) yielded a nearly pure $n=3$ phase [90, 98, 100]. The actual composition is, however, close to $\text{Tl}_{1.7}\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_2\text{O}_x$. In the case of $\text{TlCaBa}_2\text{Cu}_2\text{O}_x$ (1122) starting from a stoichiometric mixture of oxides corresponding to the ideal stoichiometry always yielded a mixture of 1122 and 2122 phases, the relative proportion of the two being dependent on the conditions. It has been demonstrated recently [101] that thallium-deficient compositions corresponding to $\text{Tl}_{1-x}\text{CaBa}_2\text{Cu}_2\text{O}_x$ ($x=0.0$ to 0.3) yield better monophasic 1122 materials.

The thallium content of the material not only determines the number of Tl-O layers but controls the hole concentration. As mentioned earlier, one of the good starting compositions to obtain $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{O}_{10}$ (2223) is $\text{TlCa}_3\text{BaCu}_2\text{O}_x$ (1313) which bears little relation to the composition of the final product. Another example is the formation of the $n=4$ phase, $\text{TlCa}_2\text{Ba}_2\text{Cu}_4\text{O}_x$ (1324). Detailed studies [102] have shown that the 2223 phase formed initially transforms to the 1223 phase with an increase in the duration of heating. After prolonged sintering, the 1324 phase is formed at the expense of the 1223 phase. Similar transformations have also been observed in the formation process of $\text{TlCa}_2\text{Ba}_2\text{Cu}_4\text{O}_x$ with five Cu-O layers [103].

The Sr analogue of $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+1}$ cannot be prepared in pure form. However, they are stabilized by

Starting composition	Temp. (K)	Conditions		Product	T_c (K)	Ref.
		...	Gas			
$Tl_2Ba_2CuO_6$	1148	3 h	Sealed gold tubes	2201 single phase	84	[88]
$Tl_2CaBa_3Cu_2O_8$	1173	6 h	Sealed gold tubes	2122 single phase	98	[88]
	1150	3 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_2Ba_3Cu_2O_8$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_3Ba_3Cu_2O_8$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_2Ba_3Cu_2O_{10}$	1173	6 h	Sealed gold tubes	2223 major phase	105	[88]
	1123	20 min	Sealed silica ampoule	2223 major phase	106	[95]
	1103	12 h				
$TlCa_3BaCu_2O_8$	1153	3 h	Sealed silica ampoules	2223 major phase	125	[100]
$Tl_2CaBa_3Cu_2O_8$	1153	3 h	Sealed silica ampoules	2223 major phase	108	[100]
$TlBa_3Ca_2Cu_2O_8$	1163	3 h	Sealed silica ampoules	1021 single phase	40	[111]
$TlSrLaCuO_3$	1170	2 h	Sealed silica ampoules	1021 single phase	40	[109]
$TlSr_{1-x}Nd_xCu_2O_8$	1170	2 h	Sealed silica ampoules	1122 major phase	80	[110]
$TlCaBa_3Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 major phase + 2122 impurity	90	[101]
$Tl_{0.8}CaBa_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 major phase	90	[101]
$(Tl_{0.5}Pb_{0.5}Ca_{1-x}Sr_xCu_2O_{2+x})$	1170	3 h	Sealed silica ampoules	1122 single phase	90	[104]
$Tl(Ca_{0.5}Y_{0.5}Sr_xCu_2O_7)$	1170	3 h	Sealed silver tubes	1122 single phase	90	[82]
$TlCa_2Ba_2Cu_2O_8$	1163	6 h	Sealed silica ampoules	1223 single phase	115	[94]
$(Tl_{0.9}Pb_{0.1}Ca_{1-x}Sr_xCu_2O_8)$	1198	3-12 h	Sealed gold tubes	1223 single phase	122	[105]
$Tl_{0.5}Pb_{0.5}Sr_xCu_2O_8$	1170	2 h	Sealed silica ampoules	1223 major phase	60	[110]

partly substituting Tl by Pb (or Bi) or Ca by yttrium or a trivalent rare earth [92, 104-107]. Thus, $Tl_{0.5}Pb_{0.5}Ca_{1-x}Sr_xCu_2O_{2+x}$ shows a T_c of ~ 90 K for $n = 2$ and ~ 120 K for $n = 3$. $TlCa_{0.5}Y_{0.5}Sr_xCu_2O_7$ also shows a T_c of 90 K. These cuprates in the Tl/Pb-Ca/Ln-Sr-Cu-O systems are prepared in a manner similar to the Tl-Ca-Ba-Cu-O system except that $SrCO_3$ is used in place of $BaCO_3$ or BaO_2 . $Sr_2Ti_2O_7$ has also been used as a starting material in some instances [97]. The $n = 1$ member, TlM_2CuO_3 ($M = Sr$ or Ba) is also stabilized by the substitution of Pb or Bi for Tl or a trivalent rare earth for Sr or Ba [108-111]. All these compounds showing a T_c of 40 K have been prepared by the matrix reaction method.

Single thallium layer cuprates of the general formula $Tl_{1-x}A_xLn_2Cu_2O_8$ with $A = Sr, Ba$; $Ln = Pr$ (Nd, Ce) as well as $Tl_{0.5}Pb_{0.5}(Ln_{1-x}Ce_x)_2Sr_2Cu_2O_8$ ($Ln = Pr, Gd$) with a fluorite-type Ln_2O_3 layer have been prepared by the ceramic method [112, 113]. The as-prepared materials are semiconductors. It has been shown by Liu *et al* [114] that annealing $TlBa_2(Eu, Ce)_2Cu_2O_8$ (1222 phase) under an oxygen pressure of 100 bar induces superconductivity with a T_c of ~ 40 K.

As in the case of bismuth cuprates, the final composition of thallium cuprates is unlikely to reflect the composition of the starting mixture. Structural studies [99, 115] have shown that there is cation disorder between Tl and Ca/Sr sites. Therefore, in order to obtain a superconducting composition corresponding to a particular copper content, one has to start with various arbitrary compositions and vary the synthesis conditions. The actual composition of the final product can be quite unexpected (e.g. $Tl_{1.83}Ba_2Ca_{1.4}Cu_2O_8$ or $Tl_{1.84}Ba_{2.01}CuO_8$) as shown by analytical electron microscopy [85]. In table 4 we have listed the pre-

parative conditions employed for the synthesis of thallium cuprates by the ceramic method.

2.6. Lead cuprates

The conditions for the synthesis of superconducting lead cuprates are more stringent than for the other copper oxide superconductors. Direct synthesis of members of the $Pb_2Sr_2(Ln, Ca)Cu_2O_{8+x}$ ($Ln = Y$ or rare earth) family by the reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 1173 K is not possible because of the high stability of $SrPbO_3$ -related perovskite oxides. Preferential loss of the more volatile PbO leads to micro-inhomogeneities. Furthermore, Pb in these compounds is in the 2+ state while part of the Cu is in the 1+ state. Synthesis has therefore to be carried out under mildly reducing conditions, typically in an atmosphere of N_2 containing 1% O_2 . The most common method that has been employed for the synthesis of these lead cuprates is the matrix reaction method [116]. For $Pb_2Sr_2(Ln, Ca)Cu_2O_{8+x}$ ($Ln = Y$ or rare earth), a mixed oxide containing all the metal ions except Pb is made by reacting $SrCO_3$, Ln_2O_3 or Y_2O_3 , $CaCO_3$, and CuO in the appropriate ratios around 1223 K in air for 16 h. The mixed oxide is then taken with an appropriate amount of PbO , ground thoroughly, pelletized and heated in the 1133-1198 K range in a flowing stream of nitrogen containing 1% O_2 for periods between 1 and 16 h. Generally, short reaction times and quenching the product from the sintering temperatures into liquid nitrogen in the same atmosphere gives better-quality samples. Even though this is the common method for preparing $Pb_2Sr_2(Ln, Ca)Cu_2O_{8+x}$, it is not always easy to obtain samples exhibiting good, reproducible

superconducting properties. The lead cuprates from the method described above generally show broad transitions in the $R-T$ curves with negative temperature coefficients of resistance above T_c .

Studies of the dependence of T_c on the calcium concentration in the $\text{Pb}_2\text{Sr}_{1-x}\text{Y}_x\text{Ca}_x\text{Cu}_2\text{O}_{6+x}$ system [117] have shown that heating the samples near the melting point between 1198 and 1228 K for 2 h and post-annealing in flowing nitrogen gas at a temperature between 673 and 773 K improves the superconducting properties of the samples dramatically. Direct one-step synthesis has been achieved [118] by reacting the metal oxides in sealed gold tubes around 1223 K. An alternative route to the direct synthesis from metal oxides and/or carbonates has also been demonstrated [119]. Superconductivity near 70 K has been reported in Ca-free $\text{Pb}_2\text{Sr}_2\text{LnCu}_2\text{O}_{6+x}$ ($\text{Ln} = \text{Y}$ or rare earth) employing the vacuum annealing procedure [120]. Substitution of Pb by Bi in $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{6+x}$ has also been carried out by the ceramic method [121]. About 30% of Pb can be substituted by Bi, and such a substitution increases the T_c up to 100 K. The $n = 0$ member of the $\text{Pb}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Ln}_x)\text{Cu}_{2+x}\text{O}_{6+2x}$ series (namely $\text{Pb}_2(\text{SrLa})\text{Cu}_2\text{O}_{6+x}$) has been prepared successfully by this matrix reaction method [122].

Unlike the 2213-type lead cuprates, superconducting 1212-type lead cuprates of the formula $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{V}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-x}$ are synthesized in an oxidizing atmosphere. Several authors have reported direct synthesis as well as reactions under closed conditions [123-127]. In the direct synthesis of these cuprates, care is taken to prevent the loss of Pb by wrapping pellets in gold or platinum foil [127]. Rouillon *et al* [125, 126] have reported the synthesis of 1212 lead cuprates by the direct reaction of the component oxides in evacuated silica ampoules. This method has

the advantage of adjusting the oxygen partial pressure required for the synthesis. Both 2213-type and 1212-type lead cuprates have been prepared using the nitrates of the metal ions as the starting materials [128]. Although this procedure yields 2213 or 1212 phases in a single step, the product obtained always has impurities such as Y_2O_3 , CuO etc.

A superconducting lead cuprate of the formula $(\text{Pb}, \text{Cu})(\text{Eu}, \text{Ce})_2(\text{Sr}, \text{Eu})_2\text{Cu}_2\text{O}_8$ (1222 phase) containing a fluorite layer has been prepared by the direct reaction of the component metal oxides at 1273 K in oxygen atmosphere [129].

High-pressure ceramic synthesis has been employed to prepare lead cuprates of the 1212 type [130, 131]. In order to prepare $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-x}$, sintering is carried out at 1213 K for 15 h under an oxygen pressure of 100 bar followed by fast cooling to 373 K. The samples obtained from high-pressure oxygen treatment show higher T_c s than those processed at 1 bar pressure of oxygen. Substitution of Y by other rare earths has been possible by this high-oxygen-pressure method [131]. All the rare-earth substituted compounds are superconducting with T_c s in the 50-70 K range. The T_c decreases with increase in the size of the rare earth. In table 5 we summarize the conditions for the synthesis of the various lead cuprates by the ceramic method.

2.7 Electron-doped superconductors

All the cuprates discussed till now are hole superconductors. Synthesis of electron-doped cuprate superconductors of the type $\text{Ln}_{2-x}\text{M}\text{CuO}_{4-x}$ ($\text{Ln} = \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}$; $\text{M} = \text{Ce}, \text{Th}$), possessing the T' structure, is generally achieved by the ceramic method [132-134]. The conditions of synthesis are more stringent since the

Table 5. Conditions for the synthesis of lead cuprates by the ceramic method.

Compound	Starting materials	Conditions			Comments	T_c (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_2\text{O}_{6+x}$	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	1143	1-36 h	$\text{N}_2 + 1\% \text{O}_2$		78	[116]
	$\text{PbO}, \text{PbO}_2, \text{Cu}_2\text{O}, \text{SrO}_2, \text{Y}_2\text{O}_3, \text{CuO}$	1223	12-48 h		Sealed gold tubes	78	[118]
	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CuO}$	1073	15 h	air			
	CaO_2, CuO	1173	2 h	air			
		1073	1-6 h	N_2		78	[119]
$\text{Pb}_2\text{Sr}_2\text{La}_{0.5}\text{Cu}_2\text{O}_{6+x}$	$\text{PbO}, \text{La}_2\text{O}_3$	1063	6 h	N_2	2202 major phase + $\text{Pb}_2\text{LaCu}_{0.5}\text{O}_7$ impurity	26	[122]
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{SrLaCuO}_4$	$\text{Sr}_2\text{CuO}_7, \text{CuO}$	1073	5 h	air			
	$\text{PbO}, \text{SrCO}_3, \text{La}_2\text{O}_3, \text{CuO}$	1278	2 h	O_2		25	[123]
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{V}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-x}$	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CaO}_2, \text{CuO}$	1123	10 h	air			
		1273	1 h	O_2	1212 major phase + $\text{Sr}_2\text{Pb}_2\text{Cu}_{0.5}\text{O}_{11}$ impurity	50	[124]
	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$ matrix	1243	3 h	O_2	1212 major phase + $\text{Sr}_2\text{Pb}_2\text{Cu}_{0.5}\text{O}_{11}$ impurity	47	[127]
$(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{V}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$	$\text{PbO}, \text{PbO}_2, \text{Sr}_2\text{CuO}_7, \text{Y}_2\text{O}_3, \text{CaO}_2, \text{Cu}_2\text{O}, \text{CuO}$	1108-1223	1-10 h		Evacuated silica tubes	100	[126]
$(\text{Pb}_{0.5}\text{Ca}_{0.5})\text{Sr}_2(\text{V}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$	$\text{PbO}_2, \text{PbO}, \text{SrO}_2, \text{SrCuO}_2, \text{Y}_2\text{O}_3, \text{CaO}, \text{CuO}$	1108-1223	1-10 h		Evacuated silica tubes	80	[126]
$(\text{Pb}_{0.5}\text{Ca}_{0.5})\text{Sr}(\text{Y}_{0.75}\text{Eu}_{0.25})\text{Cu}_2\text{O}_7$	$\text{PbO}, \text{SrCO}_3, \text{Eu}_2\text{O}_3, \text{CuO}, \text{CuO}$	1123	10 h	air	Single phase	25	[129]
		1323	1 h	O_2	1222		

material, by making sure that the extra electron donated by Ce^{2+} or Th^{2+} does not se the oxygen content of the cuprate. For this reason, samples after calcination and sintering at 1323 K in air (for 24 h) are annealed in a reducing atmosphere (typically Ar, N_2 , or dilute H_2) at 1173 K to achieve superconductivity. Samples prepared in this manner show a negative temperature coefficient of resistance above T_c in the R - T curves; the resistivity drop at T_c is also not sharp. An alternative synthetic route involves the reaction of pre-reacted $NdCeO_{3.5}$ material with the required amounts of Nd_2O_3 and CuO at 1253 K for a minimum period of 48 h in flowing oxygen [135]. The samples are then rapidly quenched from 1253 K in an argon atmosphere to achieve superconductivity. This procedure eliminates the slow diffusion of Ce throughout the Nd_2CuO_{4-x} host and gives uniform concentrations of cerium and oxygen. Samples obtained from this route show a sharp transition at 21 K.

Superconductivity with a T_c of 25 K is induced by doping fluorine for oxygen in Nd_2CuO_4 . This has been accomplished by taking NdF_3 as one of the initial reactants [136]. Substitution of either Ga or In for copper in non-superconducting $Nd_{1-x}Ce_xCuO_{4-x}$ also induces superconductivity [137, 138].

2.8. Infinite-layer cuprates

Discovery of superconductivity in cuprates containing infinite CuO_2 layers has been of great importance in understanding the phenomenon. Very high pressures have been employed for obtaining the infinite-layer cuprates. Both hole-doped (e.g. $Ca_{1-x}Sr_xCuO_2$) and electron-doped ($Sr_{1-x}Nd_xCuO_2$) infinite-layer cuprate superconductors with a maximum T_c of 110 K have been reported [139-142]. Infinite-layered cuprates of the type $Ba(Sr)CuO_{2-x}$, $(Ca, Sr)CuO_2$ are synthesized in an oxidizing atmosphere under high hydrostatic pressure [139, 140, 142]. Electron-doped $Sr_{0.88}Nd_{0.12}CuO_2$ is also prepared under high hydrostatic pressures [141]. Metal nitrates are generally used as the starting materials since carbonates of Ba, Sr and Ca have high decomposition temperatures. After decomposing the metal nitrates at around 873-1123 K in air, the product is subjected to high pressure to obtain the superconducting phases. $Sr_{0.88}Nd_{0.12}CuO_2$, which superconducts at 40 K, is made under a hydrostatic pressure of 25 kbar at 1273 K. Superconducting $(Ca, Sr)CuO_2$ is prepared at 1273 K under 6 GPa pressure. Deficiency of Sr and Ca as well as the oxidizing atmosphere make this phase superconducting, and the oxidizing atmosphere is provided by heating a capsule containing $KClO_4$ along with the sample. This cuprate has a T_c (onset) of 110 K.

3. Coprecipitation and precursor methods

Coprecipitation involves the separation of a solid containing various ionic species chemically bound to one

another. Coprecipitation of well defined stoichiometry with respect to the metal ions is obtained only when the following conditions are satisfied.

(i) The precipitating agent is a multivalent organic compound which can coordinate with more than one metal ion, and the precipitation rate is fast.

(ii) The solid precipitating out of the solution should be really insoluble in the mother liquor.

The anions generally preferred for coprecipitation of oxide materials are carbonates, oxalates, citrates etc. The same is true of high- T_c cuprates. The precipitates in some instances could be genuine precursors or solid solutions [5, 6]. It is well known that precursor solid solutions drastically bring down diffusion distances for the cations and facilitate reactions in the solid state. We shall not distinguish precursor solid solutions precipitated from solutions from other precursors in this discussion.

The precipitates (carbonate, oxalate etc) are heated at appropriate temperatures in a suitable atmosphere to obtain the desired cuprate. Some of the advantages of the coprecipitation technique over the ceramic method are an homogeneous distribution of components, a decrease in the reaction temperatures and of the duration of annealing, a higher density and a lower particle size of the final product. The major drawback of this route is the control over the stoichiometry of the final product.

3.1. $La_{2-x}Sr_xCuO_4$

La, Sr and Cu in $La_{2-x}Sr_xCuO_4$ are readily coprecipitated as carbonates [11, 12, 143]. For this purpose the required quantities of the various metal nitrates are dissolved together in distilled water. Alternatively, the corresponding oxides are dissolved in nitric acid to give a nitrate solution and the pH of the solution is adjusted to 7-8 by the addition of KOH solution. A solution of K_2CO_3 of appropriate strength is then slowly added under stirring to give a light blue precipitate which is thoroughly washed. The precipitate is dried at 420 K and calcined at 1070 K for 8 h in air. The resulting black powder is ground and pelletized and sintered at 1270 K for 16 h in air to obtain monophasic $La_{1.87}Sr_{0.13}CuO_4$ superconducting at 35 K.

Instead of as carbonate, the metal ions are also readily precipitated as oxalate by the addition of either oxalic acid or potassium oxalate to the solution of metal nitrates [11, 12, 144, 145]. The precipitated oxalate is then decomposed to obtain the cuprate. This method has certain disadvantages:

(i) La^{3+} in the presence of an alkali metal oxalate first yields lanthanum oxalate which further reacts with the precipitating agent to give a double salt. Control of stoichiometry therefore becomes difficult, leading to multiphasic products.

(ii) The relative solubilities of some of the oxalates also pose difficulties. For example, SrC_2O_4 is nearly four times more soluble than SrCO_3 .

3.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

$\text{YBa}_2\text{Cu}_3\text{O}_7$ and related 123 compounds can be obtained via coprecipitation of the component metals (from a nitrate solution) as a formate [146, 147], acetate [148], oxalate [12, 149–156], hyponitrite [157] or hydroxycarbonate [158, 159]. Some of these precipitates could be genuine precursor compounds as is indeed the case with the hyponitrite.

In oxalate coprecipitation [12, 149–152], oxalic acid solution of appropriate concentration is added to an aqueous solution of mixture of nitrates of Y, Ba and Cu and the pH of the solution is adjusted to 7.5 (by dilute NH_3). The pale green slurry thus formed is digested for 1 h, filtered and dried. The oxalate is converted to orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by heating at 1053 K in air for 5 days followed by oxygenation at 723 K. This procedure, even though successful in making superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in small particulate form, often results in undesirable stoichiometry because of the moderate solubility of barium oxalate. Furthermore, rare-earth ions in the presence of ammonium oxalate give a double salt with the excess oxalate which competes with the precipitation of copper and barium oxalates. These difficulties can be overcome either by taking a known excess (wt%) of barium and copper or by using triethylammonium oxalate as the precipitant in aqueous ethanol medium [153–155]. The alcoholic medium decreases the solubility of barium oxalate and the pH of the solution is controlled *in situ*.

A better method of homogeneous coprecipitation of oxalates is that of Liu *et al* [156] using urea and oxalic acid. Urea, on heating, is hydrolysed liberating CO_2 and NH_3 , and thus gradually adjusting the pH throughout the solution. The CO_2 liberated controls the bumping of the solution during digestion. The oxalate coprecipitation route is widely described in the literature. The reactive powders obtained by the oxalate coprecipitation method decrease the sintering temperature. The formation of BaCO_3 in the intermediate calcining step makes it difficult to obtain $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in pure form.

Complete avoidance of the formation of BaCO_3 during the synthesis is possible using the hyponitrite precursor [157]. The hyponitrite precursor is obtained from a nitrate solution of Y, Ba and Cu ions by the addition of an aqueous $\text{Na}_2\text{N}_2\text{O}_2$ solution. The precipitate is converted into superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by heating at around 973 K in an argon atmosphere, followed by oxygen annealing at 673 K. Although this route provides a convenient means of obtaining the 123 cuprate at much lower temperatures than with other methods, there is a possibility of contamination of alkali metal ions during the course of the precipitation.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ can also be prepared by the hydroxycarbonate method [158, 159]. Here, KOH and K_2CO_3

are employed to precipitate copper as the hydroxide and Y and Ba as the carbonates in the pH range of 7–8. By employing NaOH and Na_2CO_3 , complete precipitation as hydroxycarbonate is attained at a pH of ~13. The product from the above two procedures is homogeneous, showing sharp onset of superconductivity at 92 K. The possibility of contamination by alkali metal ions cannot, however, be avoided.

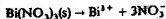
3.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

$\text{YBa}_2\text{Cu}_4\text{O}_8$ can be prepared by the oxalate route [160] wherein the solution of Y, Ba and Cu nitrates in water is added dropwise into oxalic acid–triethylamine solution under stirring. Complete precipitation of Y, Ba and Cu with the desired stoichiometry of 1:2:4 is achieved in the pH range of 9.3–11.3. The precipitated oxalates are filtered and dried in air at 393 K. The solid obtained is then heated in the form of pellets at 1078 K in flowing oxygen for 2–4 days. The product after quenching in air shows the 124 phase as the major product with a T_c of 79 K.

An alternative coprecipitation route for the synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ is the method of Chen *et al* [161] in which the aqueous nitrate solution of the constituent metal ions is mixed with 8-hydroxyquinoline-triethylamine solution. The precipitated oxine is filtered, washed, dried and sintered at 1088 K in oxygen for 3 days to yield phase-pure $\text{YBa}_2\text{Cu}_4\text{O}_8$ showing a T_c of 80 K. Ethylenediaminetetraacetic acid [161] as well as carbonate routes [162] have also been employed for the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$. Coprecipitation using triethylammonium oxalate has been exploited for substituting Sr in place of Ba in $\text{YBa}_2\text{Cu}_4\text{O}_8$ [163].

3.4. Bismuth cuprates

Very few coprecipitation studies have been carried out on the preparation of bismuth cuprates. One reason may be that despite the good sample homogeneity generally obtained through solution methods, the chemistry of bismuth cuprates is rather complex. It is not that easy to find compounds of all the constituent metal ions soluble in a common solvent; controlling the stoichiometry in these cuprates is also difficult in the coprecipitation procedure. Furthermore, bismuth nitrate, which is often used as one of the starting materials, decomposes in cold water to a basic nitrate precipitate as given by



This problem can be overcome to some extent by preparing the nitrate solution of bismuth in nitric acid or by starting with bismuth acetate instead of the nitrate.

Bidentate ligands such as the oxalate are found to react more rapidly than multidentate ligands such as citric acid [164–174] in the coprecipitation process. Complexes of oxalic acid are also more stable than

the stoichiometry because of the relative solubility of $\text{Bi}_2\text{C}_2\text{O}_7$ or SrC_2O_4 .

A straightforward oxalate coprecipitation is achieved by dissolving the acetates of Bi, Ca, Sr and Cu in glacial acetic acid and then adding excess oxalic acid to the solution [164]. The oxalate precipitate is dried and decomposed at around 1073 K in air and processed in the 1103–1123 K range for periods ranging from 24 h to 4 days, depending on the starting composition. The $n = 2$ (2222) member obtained by this procedure shows zero resistance at 83 K. In another procedure reported by Zhang *et al* [165], first the Sr/Ca/Cu nitrate solutions are mixed in the required molar ratio. Into this solution is poured a solution of bismuth nitrate prepared in nitric acid along with oxalic acid. The complete precipitation occurs at a pH of around 5 (attained by the addition of aqueous NaOH). This process involves the possibility of contamination of sodium ions; this has been circumvented by using $\text{N}(\text{CH}_3)_4\text{OH}$ to adjust the pH of the solution [166] and complete precipitation of the oxalates occurs at a pH of 12. All these procedures, however, produce mixed-phase samples.

For the preparation of the monophasic lead-doped $n = 3$ member (2223), oxalate coprecipitation has been found effective [167–174]. In the procedure reported by Chiang *et al* [171], the molar ratio of the chelating agent (oxalic acid) and the nitrate anions (from the metal nitrate solutions) is fixed at 0.5 and the pH, adjusted by NH_4OH solution, at which complete precipitation occurs is 6.7. The product from this method, $\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_7$, after sintering at 1133 K in air for 72 h, shows a T_c of 110 K.

Coprecipitation as oxalates to prepare the lead-doped $n = 3$ member (2223) has been achieved from an ethylene glycol medium using triethylammonium oxalate and oxalic acid [172]. A more easily controlled and reproducible oxalate coprecipitation procedure appears to be that of Shi *et al* [173] where in a mixture of triethylamine and oxalic acid is employed. The advantage of using triethylamine is that it has a higher basicity and a lower complexing ability towards Cu(II) than has ammonia. Control of the stoichiometry of the final product is therefore better obtained with this procedure; precipitation occurs in the pH range 1.5–2.2. The coprecipitated oxalates sintered at 1133 K in air for a minimum period of 72 h give monophasic $\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{10}$ with a T_c of 110 K. It is possible to avoid adjusting the pH in the coprecipitation of oxalates [174]. The procedure involves coprecipitating the oxalates from dilute acetate solutions instead of from nitrate solutions. The oxalates are then converted to nearly phase-pure $\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{10}$ (T_c of 106 K) by sintering at 1123 K in air for 160 h.

Carbonate coprecipitation has also been carried out for the synthesis of superconducting bismuth cuprates [175, 176], but the method does not yield monophasic products.

Coprecipitation of the $n = 3$ cuprates from aqueous solutions as oxalates is hindered by the solubility of thallium oxalate. However, Bernhard and Gritzer [177] have found that complete coprecipitation as oxalates can be achieved by starting with thallium acetate in glacial acetic acid medium. In the procedure reported for the preparation of the $n = 3$ member (2223), stoichiometric amounts of thallium acetate, CaCO_3 , BaCO_3 and copper acetate are dissolved in water containing glacial acetic acid. The solution containing all the cations is then added to a solution of oxalic acid (excess) under stirring. The precipitate, after digestion for 1 h, is filtered, washed and dried. The oxalates are heated in the form of pellets (wrapped in gold foil) at around 1173 K for 6 min in an oxygen atmosphere. The product after annealing in the same atmosphere shows 2223 as the major phase with a T_c of 118 K.

3.6. Lead cuprates

Carbonate coprecipitation is found to be satisfactory for the synthesis of representative members of superconducting lead cuprates [128] of 2213 and 1212 types, namely $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{8+x}$ and $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-x}$. Coprecipitation as carbonates has been achieved by adding the nitrate solution of the constituent metal ions to an aqueous solution of sodium carbonate (in excess) under constant stirring. The carbonate precipitate thus obtained is washed and dried. The decomposed powder is heated in the form of pellets around 1153 K in a suitable atmosphere. $\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_2\text{O}_{8+x}$ obtained by this method after heating for 4 h in nitrogen containing 1% O_2 showed 2213 as the major phase ($T_c \sim 74$ K) with impurities such as Y_2O_3 , CuO . The 1212 phase obtained after heating in oxygen at 1153 K for 12 h showed a broad transition with a T_c (onset) of 100 K. This method has the advantage of single heating rather than the multistep procedures required in the other methods.

4. Sol-gel process

The sol-gel process is employed in order to get homogeneous mixing of cations on an atomic scale so that the solid state reaction occurs to completion in a short time and at the lowest possible temperature. The term sol often refers to a suspension or dispersion of discrete colloidal particles, while a gel represents a colloidal or polymeric solid containing a fluid component which has the internal network structure wherein both the solid and the fluid components are highly dispersed. In the sol-gel process a concentrated sol of the reactant oxides or hydroxides is converted to a semi-rigid gel by removing the solvent. The dry gel is heated at an appropriate

temperature to obtain the product. Most of the reactions in the sol-gel process occur via hydrolysis and polycondensation.

Two different routes for the sol-gel process are usually described in the literature for the synthesis of high- T_c cuprate superconductors:

- (i) Via molecular precursors (e.g. metal alkoxides) in organic medium;
- (ii) Via ionic precursors in aqueous medium (citrate gel process).

The purity, microstructure and physical properties of the product are controlled by varying the precursor, solvent, pH, firing temperatures and atmosphere of heat treatment.

4.1. 214 Cuprates

Superconducting 214 compounds are prepared both by means of organometallic precursor [178] and by the citrate gel process [11]. Lanthanum 2,4-pentanedionate, barium 2,4-pentanedionate and copper (II) ethyl hexanoate are mixed at room temperature in the appropriate ratios in methoxyethanol medium to obtain the organometallic precursor. After vigorous stirring at room temperature, the precursor gel is converted to monophasic $\text{La}_{1-x}\text{Ba}_x\text{CuO}_4$ (T_c 23 K) by firing at 873 K in oxygen.

In the citrate gel process, a mixture of citric acid and ethylene glycol is added to the solution containing the required quantities of metal nitrates. The resulting solution is vigorously stirred and heated around 393 K. During this process, oxides of nitrogen evolve, resulting in a viscous gel. The gel is decomposed at 673 K in air and the resulting black powder is then given the necessary heat treatment to obtain the superconducting oxide.

4.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, the alkoxide precursors are both very expensive and difficult to obtain. In addition, the solubility of copper alkoxides is very low in organic solvents and yttrium alkoxides are readily hydrolysed even by a trace of water. Despite these difficulties, superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been prepared using alkoxides [157, 179–181]. A simple reaction involving $\text{Y}(\text{OCHMe}_2)_3$, $\text{Ba}(\text{OCHMe}_2)_2$ and $\text{Cu}(\text{NBu}_2)_2$ in THF in an argon atmosphere gives the organometallic precursor [157]. The precursor powder, after removal of the solvent, is sintered at 973 K in flowing argon to obtain tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Following oxygenation at 673 K, the product shows a T_c of 85 K. Superconducting properties have been improved by using *n*-butoxides of Y, Ba and Cu in butanol solvent [179].

Alternatively, methoxyethoxides of yttrium, barium and copper have been used as precursors in methoxyethanol-methylethylketone-toluene solvent mixture to prepare $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [180]. In some of the preparations, $\text{Cu}(\text{NO}_3)_2$ (soluble in ethanol) or copper

acetylacetonate (soluble in toluene) is used along with the alkoxides of yttrium and barium to overcome the problem of low solubility of copper alkoxides [182, 183]. Organometallic precursors involving propionates [153] and neodecates [184] have also been used for preparing $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

Modified sol-gel methods which do not involve the metal alkoxide precursors have been employed by many workers. Thus, Nagano and Greenblatt [185] have employed metal nitrates dissolved in ethylene glycol. After refluxing around 353 K under vigorous stirring, a bluish green colloidal gel is obtained. The gel is converted into orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by heating to 1223 K in flowing oxygen. Precipitating all the three ions as hydroxides also results in fine colloidal particles of the starting materials [186–188]. The precipitation is generally carried out by the addition of NH_4OH [186], $\text{N}(\text{CH}_3)_4\text{OH}$ [187] or $\text{Ba}(\text{OH})_2$ [188] to a solution of metal nitrates (pH range 7–8). These hydroxides are decomposed around 1223 K in oxygen to give $\text{YBa}_2\text{Cu}_3\text{O}_7$, showing a T_c of 93 K.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been prepared by the citrate gel process [189–193]. In this method 1 g equivalent of citric acid is added to each gram equivalent of the metal. The pH of the solution is adjusted to around 6 (either by NH_4OH or by ethylenediamine). Evaporation of the solvent (water) around 353 K, results in a viscous dark blue gel. The gel is decomposed and the powder sintered in the form of pellets at 1173 K in oxygen to obtain orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 93$ K). By this method, ultrafine homogeneous powders (particle size $\sim 0.3 \mu\text{m}$) are obtained. The crucial step in this process is the adjustment of the pH which controls the stoichiometry of the final product. This limitation has been overcome by dispersing the citrate metal ion complexes in a solvent mixture of ethylene glycol and water [194, 195].

Problems such as the formation of BaCO_3 during the calcination step, filtration and contamination of alkali metal ions in the final product are avoided in the sol-gel process. Furthermore, perfect homogeneity is obtained before calcination. The sol-gel process (e.g. citrate process) has the advantage over the other methods in that the gel can be used for making thick and thin superconducting films, fibres etc which have technological importance [179, 185, 186, 196–198].

4.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

The sol-gel method offers a good alternative to the ceramic method for the synthesis of superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$. The following procedure has been used to prepare $\text{YBa}_2\text{Cu}_4\text{O}_8$ at 1 atm oxygen pressure [199]. Appropriate quantities of $\text{Y}(\text{n-OC}_2\text{H}_5)_3$, $\text{Ba}(\text{s-OC}_2\text{H}_5)_2$ and $\text{Cu}(\text{s-OBu})_2$ in butanol-xylene mixture are refluxed in an argon atmosphere at 343 K for a period of 30 h. The fine powder after the vigorous reaction is freed from the solvent and dried. The powder is heated in the form of pellets at 1033 K in flowing oxygen to obtain superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$.

used as the source of copper in this process [200].

In the modified citrate gel process, to prepare $\text{YBa}_2\text{Cu}_3\text{O}_x$ [201, 202], 1 g equivalent of citric acid is added for each gram equivalent of the metal and the pH of the solution is adjusted to ~ 5.5 by the addition of ethylenediamine. The resulting clear solution is evaporated to yield a viscous purple gel. The decomposed gel is sintered in flowing oxygen for 3–5 days at 1088 K to obtain nearly monophasic $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($T_c = 66$ K). Kakihana *et al* [203] have reported the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_x$ using a precursor obtained from citrate metal ion complexes uniformly dispersed in a solvent mixture of ethylene glycol and water. This method yields phase-pure $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($T_c \sim 79$ K) and eliminates the need to adjust the pH.

4.4. Bismuth cuprates

There have been very few reports of the preparation of bismuth-based cuprate superconductors by the alkoxo sol-gel method [204]. Some of the difficulties arise because the relevant bismuth/lead alkoxides are not readily available; it is also not easy to get a common organic solvent to dissolve the various metal alkoxides simultaneously. Dhalke *et al* [204] have, however, attempted to synthesize the lead-doped $n = 3$ member (2223) using organometallic precursors involving propionates. The starting materials were taken in the form of nitrates and converted into propionates by the addition of an excess of 100% propyl alcohol. This step was followed by the addition of ammonium hydroxide and ethylene glycol to increase the alkoxo anion concentration, thus in turn increasing the viscosity of the solution. All the solutions were mixed together and dried at 353 K. The resin after calcination at 1123 K in air and sintering at 1118 K gave a mixture of the $n = 3$ and $n = 2$ members.

A simple sol-gel method involving the addition of dilute ammonia to an aqueous solution containing nitrates of Bi, Sr and acetates of Ca, Cu and Pb (until the pH of the solution reached around 5.5) has also been employed to prepare bismuth cuprates [205, 206]. The blue solution after concentrating at around 343 K gives a viscous gel. The gel is decomposed and the powder sintered at around 1128 K in air. The product from this procedure is multiphasic showing a T_c of 104 K. The simplicity of the method and the formation of the $n = 3$ phase in a short time makes it somewhat superior to the conventional ceramic route. The modified citrate gel process has been employed to prepare the $n = 2$ member (2212) in pure form with a T_c of 78 K [193].

4.5. Lead cuprates

The modified citrate gel process has been successfully employed by Mahesh *et al* [207] for the synthesis of lead cuprates of the 2213 or 1212 type. In a typical procedure, a mixture of citric acid and ethylene glycol in

is concentrated at 373 K to get a viscous gel. The gel after decomposition is heated in the form of pellets in the temperature range of 1073–1173 K either in N_2 containing 1% O_2 or in an oxygen atmosphere. $\text{Pb}_2\text{Sr}_2\text{Y}_2\text{O}_{10}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$ obtained from this process shows a sharp superconducting transition at 70 K. The 1212 cuprate also shows a sharp transition at 60 K. This process is superior to the ceramic procedure for synthesizing superconducting lead cuprates.

5. Alkali flux method

Strong alkaline media, either in the form of solid carbonate fluxes, molten hydroxides or highly concentrated alkali solutions can be employed for the synthesis of high- T_c cuprate superconductors. The alkali flux method takes advantage of both the moderate temperatures of the molten media (453–673 K) as well as of the acid-base characteristics of molten hydroxides to simultaneously precipitate oxides or oxide precursors such as hydroxides or peroxides of the constituent metals. The method stabilizes higher oxidation states of the metal by providing an oxidizing atmosphere.

Employing fused alkali hydroxides, Ham *et al* [208] have synthesized superconducting $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{K}$ or Na or vacancy) at relatively low temperatures (470–570 K). In this method, stoichiometric quantities of La_2O_3 and CuO are added to a molten mixture containing KOH and NaOH (in an approximately 1:1 ratio) in a Teflon crucible and heated at around 570 K in air for 100 h. The 1:1 mixture of KOH and NaOH melts at 440 K and since the alkali hydroxides generally contain some water, the melt is acidic and can readily dissolve oxides such as La_2O_3 and CuO . The black crystals obtained from the reaction (after washing away the excess hydroxide with water) show a T_c of 35 K. Since the reaction is carried out in alkali hydroxides, incorporation of Na^+ or K^+ ions for La^{3+} in the lattice of La_2CuO_4 cannot be ruled out. It should be noted that superconducting alkali-doped La_2CuO_4 is normally prepared at higher temperatures in sealed gold tubes [209]. Recently, alkaline hypobromite oxidation has been employed to obtain $\text{La}_2\text{CuO}_{4+x}$ with a T_c of 44 K [210].

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c \sim 88$ K) has also been prepared using the fused eutectic of sodium and potassium hydroxides in a similar manner to that described above [211]. The problem of contamination of alkali metals in the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been overcome by using the $\text{Ba}(\text{OH})_2$ flux [211]. The procedure involves heating a mixture containing stoichiometric amounts of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in an open ceramic crucible at around 1023 K in air for a short time (about 10 min) and then slowly cooling the melt to room temperature. Since $\text{Ba}(\text{OH})_2$ has two hydration states, one melting at 351 K and the other at 681 K, the lower-melting hydrate acts as the solvent for the nitrates of copper

and yttrium while the high-melting hydrate serves as the medium for intimate mixing of the reactants. The precipitate obtained from the melt, after washing with water, is sintered in air at around 1173 K followed by oxygenation at 773 K. This method yields an orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase (with little CuO impurity) showing a T_c of 92 K.

The flux method eliminates the need for mechanical grinding and introduction of carbon-containing anions, which is often encountered in the solution routes. Furthermore, the method is efficient and cost-effective.

6. Combustion method

Although many of the solution routes discussed earlier yield homogeneous products, the processes involved are quite complex. Combustion synthesis or self-propagating high-temperature synthesis (SHS), first developed by Merzhanov and Borovinskaya [212], provides a simple and rapid means of preparing inorganic materials, many of which are technologically important. Combustion synthesis is based on the principle that the heat energy liberated by many exothermic non-catalytic solid-solid or solid-gas reactions can self-propagate throughout the sample at a certain rate. This process can therefore occur in a narrow zone which separates the starting substances and reaction products.

Self-propagating combustion has been employed recently in this laboratory to synthesize members of almost all families of cuprate superconductors (except for the thallium cuprates) [213]. The method involves the addition of an appropriate fuel to a solution containing the metal nitrates in the proper stoichiometry. The ratio of the metal nitrates to the fuel is such that when the solution is dried at around 423 K, the solid residue undergoes flash combustion, giving an ash containing the mixture of oxides in the form of very fine particles (particle size 0.3–0.5 μm). The ash is then given proper heat treatment under the desired atmosphere to obtain the cuprate. The small particle size of the ash facilitates the reaction between the metal oxides due to smaller diffusion distances between the cations. Fuels such as urea [213, 214], glycine [213, 215] and tetraformal triazine (TFTA) [216] are generally employed for synthesizing cuprate superconductors. Ultrafine particles of copper metal can also act as an internal fuel wherein the combustion is initiated by flashing a laser beam for a short time [217]. Some of the cuprate superconductors which have been prepared [213] by this route include $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($T_c = 35$ K), $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($T_c = 90$ K), $\text{YBa}_2\text{Cu}_3\text{O}_8$ ($T_c = 80$ K), $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ ($T_c = 85$ K), $\text{Pb}_2\text{Sr}_2\text{Y}_{0.8}\text{Ca}_{0.5}\text{Cu}_2\text{O}_8$ ($T_c = 60$ K) and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ($T_c \sim 30$ K).

7. Other methods

In addition to the various synthetic methods discussed hitherto, a few other methods such as spray drying [218–221], freeze drying [186, 222, 223], use of metallic precursors [224, 225] and electrochemical methods

[226, 227] have also been employed for the preparation of cuprate superconductors in bulk form. In spray drying, a solution containing the metallic constituents, usually in the form of nitrates, is sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously, leaving behind an intimate mixture of the reactants which on heating at the desired temperature in a suitable atmosphere yields the cuprate. Some of the superconducting cuprates prepared by this method include $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($T_c = 91$ K) [218], $\text{YBa}_2\text{Cu}_3\text{O}_8$ ($T_c = 81$ K) [219] and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_2\text{O}_{10}$ ($T_c = 101$ K) [220, 221]. In freeze drying, the reactants (in a common solvent) are frozen by immersing in liquid nitrogen. The solvent is removed at low pressures to obtain the initial reactants in fine powder form, and these are then processed at an appropriate temperature. For example, $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($T_c = 87$ K) [186], $\text{YBa}_2\text{Cu}_3\text{O}_8$ ($T_c = 79$ K) [222] and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_2\text{O}_8$ ($T_c = 101$ K) [223] have been prepared by this method.

Metallic precursors have been used in the preparation of 123 and 247 cuprates [224, 225]. For example, oxidizing an Er–Ba–Cu alloy around 1170 K gives superconducting $\text{ErBa}_2\text{Cu}_3\text{O}_x$ with a T_c of 87 K [224]. Similarly $\text{Yb}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$ has been obtained by heating an alloy composition of YbBa_2Cu_3 (with 33 wt% of silver) under 1 atm oxygen at 1173 K [225].

Making use of electrochemical oxidation, $\text{La}_2\text{CuO}_{4+x}$ with a T_c of 44 K has been prepared at room temperature, which is otherwise possible only by use of high oxygen pressures [226, 227].

8. Oxygen non-stoichiometry

Oxygen stoichiometry plays a crucial role in determining the superconducting properties of many of the cuprates. Thus, stoichiometric La_2CuO_4 is an insulator, while an oxygen-excess material prepared under high oxygen pressures shows superconductivity with a T_c of 35 K [15]. The same holds for the next member of the homologous family, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ which is superconducting only when there is an oxygen excess [17]. The excess oxygen donates holes in these two systems. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, oxygen can be easily removed giving rise to tetragonal non-superconducting $\text{YBa}_2\text{Cu}_3\text{O}_6$. The $\text{YBa}_2\text{Cu}_3\text{O}_6$ material can be prepared by heating $\text{YBa}_2\text{Cu}_3\text{O}_x$ in an argon atmosphere at 973 K for extended periods of time [228]. The variation of T_c with oxygen stoichiometry, δ , is well known [229, 230]. When δ reaches 0.5, there is an intergrowth of $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_8$, and at this composition, the material shows a T_c of 45 K. The $\delta = 0.5$ composition is obtained by quenching $\delta \approx 0$ material, heated in a nitrogen atmosphere at 743 K [231]. Similarly, by quenching $\text{YBa}_2\text{Cu}_3\text{O}_x$ at 783 K in air, $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ (showing a T_c of ~ 60 K) is prepared [231]. The T_c of 90 K is found only when $\delta < 0.2$. $\text{YBa}_2\text{Cu}_3\text{O}_8$ is readily oxidized back to $\text{YBa}_2\text{Cu}_3\text{O}_7$. It may be noted that this oxidation-reduction process in

Cuprate	T_c (approx.)	Methods of synthesis*
$La_{2-x}Sr_x(Ba)CuO_4$	35	Ceramic*, sol-gel, combustion, coprecipitation
$La_2Ca_{1-x}Sr_xCu_2O_6$	60	Ceramic (high O_2 pressure)*
La_2CuO_{4+x}	40	Ceramic (high O_2 pressure)* alkali-flux, hypobromite*
$YBa_2Cu_3O_{7-\delta}$	90	Ceramic (annealing in O_2)*, sol-gel*, coprecipitation*, combustion
$YBa_2Cu_3O_{8-x}$ *	80	Ceramic (high O_2 pressure), ceramic (with Na_2O_2)* sol-gel*, coprecipitation*
$Bi_2CaSr_2Cu_2O_8$	90	Ceramic (air-quench)* sol-gel*, combustion, melt (glass) route*
$Bi_2Ca_2Sr_2Cu_2O_{10}$	110	Ceramic*, sol-gel, melt route
$TiCaBa_2Cu_2O_{8+x}$ *	90	Ceramic (sealed Ag/Au tube)*
$TiCa_2Ba_2Cu_2O_{8+x}$ *	115	Ceramic (sealed Ag/Au tube)*
$Tl_2Ba_2CuO_6$	90	Ceramic (sealed Ag/Au tube)*
$Tl_2CaBa_2Cu_2O_8$	110	Ceramic (sealed Ag/Au tube)*
$Tl_2Ca_2Ba_2Cu_2O_{10}$	125	Ceramic (sealed Ag/Au tube)*
$Tl_2Pb_{0.5}Ca_{0.5}Sr_2Cu_2O_{8+x}$	90	Ceramic (sealed Ag/Au tube)*
$Pb_2Sr_2Ca_{1-x}Y_xCu_2O_8$	70	Ceramic (low O_2 partial pressure)*, sol-gel* (low O_2 partial pressure)
$Pb_{0.8}Cu_{0.8}Sr_{0.5}Y_{0.5}Ca_{0.8}Cu_2O_7$	45	Ceramic (flowing O_2)*
$Hd_{2-x}Ce_xCuO_6$	30	Ceramic (low O_2 partial pressure)*
$Ca_{1-x}Sr_xCuO_2$	40-110	Coprecipitation (low O_2 partial pressure)*
$Sr_{1-x}Nd_xCuO_2$	40-110	Ceramic (high pressures)*
		Ceramic (high pressures)*

* Recommended methods are indicated by asterisks.

* Other rare-earth compounds of this type are also prepared by similar methods. Oxygen annealing is done below the orthorhombic-tetragonal transition.

* Sr analogues of these compounds with different substitutions at Ca and Ti sites are prepared by a similar procedure.

$YBa_2Cu_3O_{7-\delta}$ is of topochemical character. The other analogous rare-earth 123 cuprates also behave in a similar way with respect to the variation of T_c with T_c [237].

While $YBa_2Cu_3O_8$ has high oxygen stability, $Y_2BaCu_3O_{15-x}$ shows a wide range of oxygen stoichiometry ($0 \leq \delta \leq 1$) [233]. The maximum T_c of 90 K is achieved when δ is close to zero, and when δ reaches unity the material shows a T_c of 30 K; there is no structural phase transition accompanying the variation in oxygen stoichiometry. Usually, both yttrium 124 and 247 cuprates and their rare-earth analogues, prepared by the ceramic method under 1 atm oxygen pressure, show δ close to zero.

Bismuth cuprates of the type $Bi_2(Ca, Sr)_{1-x}Cu_3O_{8+x}$ are best prepared by quenching the samples in air or by annealing in a nitrogen atmosphere at appropriate temperatures [53, 234]. Heating the samples in an oxygen atmosphere is no good, possibly because the extra oxygen may add on to the Bi-O layers. In the case of the lead-doped $n=3$ member [2223], preparing the samples under low partial pressures of oxygen is found to increase the volume fraction of the superconducting phase [235, 236]. The $n=1$ member, $Bi_2Sr_2CuO_{8+x}$ shows metallic behaviour when there is excess oxygen [237]. By annealing in a reducing atmosphere (Ar or N_2), the excess oxygen can be removed to induce superconductivity.

Oxygen stoichiometry has a dramatic influence on the superconducting properties of thallium cuprates [94, 108, 109, 238-246]. For example, thallium cuprates of the $TlCa_{1-x}Ba_2Cu_3O_{2+x}$ family, derivatives of the

$TlCa_{1-x}Sr_2Cu_3O_{2+x}$ family and $Tl_2Ba_2CuO_6$ often have excess oxygen when prepared in sealed tubes. By annealing these samples in a reducing atmosphere (Ar, dilute H_2 , N_2 or vacuum) at appropriate temperatures, the excess oxygen is removed to induce superconductivity in some cases [108, 109, 238]. Annealing at low oxygen partial pressures or in a reducing atmosphere also increases the T_c of some of the superconducting thallium cuprates to higher values by decreasing the oxygen content [94, 239-246]. These variations are clearly related to the hole concentration where the number of holes decreases by removing excess oxygen, thereby giving the optimal concentration required for maximal T_c [247].

In lead cuprates of the $Pb_2Sr_2(La, Ca)Cu_3O_{8+x}$ (2213) type, increasing the oxygen content of the material by annealing in an oxygen atmosphere oxidizes the Pb^{2+} and Cu^{1+} without affecting the CuO_2 sheets, which governs the superconductivity in this material [248]. Though this system shows a wide range of oxygen stoichiometry (associated with a structural phase transition from orthorhombic to tetragonal symmetry), maximum T_c is observed for any given composition where δ is close to zero [249]. Samples with $\delta \approx 0$ are therefore prepared by annealing in a nitrogen atmosphere containing little oxygen. The lead 1212 cuprates, on the other hand, are best prepared in a flowing oxygen atmosphere. The samples obtained after the oxygen treatment are often not superconducting since there is an oxygen excess. The samples are quenched in air at around 1073 K in order to achieve superconductivity [250].

Superconducting properties of the electron-doped superconductors, $\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4-x}$, are sensitive to the oxygen content. The as-prepared samples which are semiconducting have oxygen content greater than four. Samples with oxygen content less than four are obtained by annealing in a reducing atmosphere (N_2 , Ar or dilute H_2) at around 1173 K. Maintaining the oxygen stoichiometry at less than four is essential for having an oxidation state of Cu less than 2+ in this material [251].

9. Concluding remarks

In the earlier sections we presented details of the preparative methods for the synthesis of various families of cuprate superconductors. In addition, we also examined the advantages and disadvantages of the different methods. Since more than one method of synthesis has been employed for preparing any given cuprate, it becomes necessary to make the right choice of method in any given situation. In order to assist in making such a choice, we have tabulated in table 6 the important preparative methods employed to synthesize some of the representative cuprates, where the recommended methods are also indicated.

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BRIEF ATTACHMENT AC

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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P.O. Box 1450
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THIRD SUPPLEMENTAL AMENDMENT

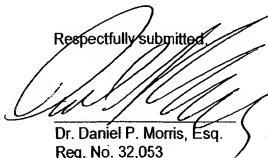
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Respectfully submitted



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ATTACHMENT AC



HIGH TEMPERATURE

C. N. R. Rao and A. K. Raychaudhuri

The following tables give properties of a number of high temperature **superconductors**. Table 1 lists the crystal structure (space group and lattice constants) and the critical transition temperature T_c for the more important high temperature **superconductors** so far studied. Table 2 gives energy gap, critical current density, and penetration depth in the superconducting state. Table 3 gives electrical and thermal properties of some of these materials in the normal state. The tables were prepared in November 1992 and updated in November 1994.

REFERENCES

1. Ginsburg, D.M., Ed., *Physical Properties of High-Temperature Superconductors*, Vols. I—III, World Scientific, Singapore, 1989—1992.
2. Rao, C.N.R., Ed., *Chemistry of High-Temperature Superconductors*, World Scientific, Singapore, 1991.
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7. Antipov, E.V. et al., *Physica*, C215, 1—10, 1993.

HIGH TEMPERATURE SUPERCONDUCTORS

C. N. R. Rao and A. K. Raychaudhuri

The following tables give properties of a number of high temperature superconductors. Table 1 lists the crystal structure (space group and lattice constants) and the critical transition temperature T_c for the more important high temperature superconductors so far studied. Table 2 gives energy gap, critical current density, and penetration depth in the superconducting state. Table 3 gives electrical and thermal properties of some of these materials in the normal state. The tables were prepared in November 1992 and updated in November 1994.

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Table 1
Structural Parameters and Approximate T_c Values of High-Temperature Superconductors

Material	Structure	T_c /K (maximum value)
$\text{La}_2\text{CuO}_{4.8}$	Bmab; $a = 5.355$, $b = 5.401$, $c = 13.15 \text{ \AA}$	39
$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_{1-x}\text{CuO}_4)$	14/mmm; $a = 3.779$, $c = 13.23 \text{ \AA}$	35
$\text{La}_{2-x}\text{Ca}_x\text{Sr}_x\text{CuO}_4$	14/mmm; $a = 3.825$, $c = 19.42 \text{ \AA}$	60
$\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821$, $b = 3.885$, $c = 11.676 \text{ \AA}$	93
$\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$	Ammm; $a = 3.84$, $b = 3.87$, $c = 27.24 \text{ \AA}$	80
$\text{Y}_2\text{BaCuO}_{15}$	Ammm; $a = 3.851$, $b = 3.869$, $c = 50.29 \text{ \AA}$	93
$\text{Bi}_2\text{Sr}_2\text{CuO}_8$	Amaa; $a = 5.362$, $b = 5.374$, $c = 24.622 \text{ \AA}$	10
$\text{Bi}_2\text{CaSr}_2\text{CuO}_8$	A ₂ aa; $a = 5.409$, $b = 5.420$, $c = 30.93 \text{ \AA}$	92
$\text{Bi}_2\text{CaSr}_2\text{CuO}_{10}$	A ₂ aa; $a = 5.339$, $b = 5.40$, $c = 37 \text{ \AA}$	110
$\text{Bi}_2\text{Sr}_2(\text{La}_{1-x}\text{Ce}_x)\text{CuO}_{10}$	P4/mmm; $a = 3.888$, $c = 17.28 \text{ \AA}$	25
$\text{Ti}_2\text{Ba}_2\text{CuO}_8$	A ₂ aa; $a = 5.468$, $b = 5.472$, $c = 23.238 \text{ \AA}$; 14/mmm; $a = 3.866$, $c = 23.239 \text{ \AA}$	92
$\text{Ti}_2\text{CaBa}_2\text{CuO}_8$	14/mmm; $a = 3.855$, $c = 29.318 \text{ \AA}$	119
$\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{CuO}_{10}$	14/mmm; $a = 3.85$, $c = 35.9 \text{ \AA}$	128
$\text{Ti}(\text{BaLa})\text{CuO}_5$	P4/mmm; $a = 3.83$, $c = 9.55 \text{ \AA}$	40
$\text{Ti}(\text{SrLa})\text{CuO}_5$	P4/mmm; $a = 3.7$, $c = 9 \text{ \AA}$	40
$(\text{Th}_x\text{Pb}_{1-x})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738$, $c = 9.01 \text{ \AA}$	40
$\text{TiCaBa}_2\text{CuO}_7$	P4/mmm; $a = 3.856$, $c = 12.754 \text{ \AA}$	103
$(\text{Th}_x\text{Pb}_x)\text{CaSr}_2\text{CuO}_7$	P4/mmm; $a = 3.80$, $c = 12.05 \text{ \AA}$	90
$\text{TiSr}_2\text{Y}_{1-x}\text{Ca}_x\text{CuO}_5$	P4/mmm; $a = 3.80$, $c = 12.10 \text{ \AA}$	90
$\text{TiCa}_2\text{BaCuO}_9$	P4/mmm; $a = 3.853$, $c = 15.913 \text{ \AA}$	110
$(\text{Th}_x\text{Pb}_x)\text{Sr}_2\text{Cu}_2\text{CuO}_9$	P4/mmm; $a = 3.81$, $c = 15.23 \text{ \AA}$	120
$\text{TiBa}_2(\text{La}_{1-x}\text{Ce}_x)\text{CuO}_5$	14/mmm; $a = 3.8$, $c = 29.5 \text{ \AA}$	40
$\text{Pb}_2\text{Sr}_2\text{La}_2\text{Cu}_2\text{CuO}_5$	Cmmm; $a = 5.435$, $b = 5.463$, $c = 15.817 \text{ \AA}$	70
$\text{Pb}_2(\text{SrLa})_2\text{CuO}_5$	P2 ₂ 2 ₁ ; $a = 5.333$, $b = 5.421$, $c = 12.609 \text{ \AA}$	32
$(\text{PbCu})\text{Sr}_2(\text{LaCa})\text{CuO}_7$	P4/mmm; $a = 3.820$, $c = 11.826 \text{ \AA}$	50
$(\text{PbCu})\text{Sr}(\text{Eu})(\text{EuCe})\text{CuO}_7$	14/mmm; $a = 3.817$, $c = 29.01 \text{ \AA}$	25
$\text{Nd}_2\text{CeCuO}_4$	14/mmm; $a = 3.95$, $c = 12.07 \text{ \AA}$	30
$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_4$	P4/mmm; $a = 3.902$, $c = 3.35 \text{ \AA}$	110
$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942$, $c = 3.393 \text{ \AA}$	40
$\text{Ba}_{0.9}\text{K}_{0.1}\text{BiO}_3$	Pm3m; $a = 4.287 \text{ \AA}$	31
$\text{Rb}_2\text{CsCuO}_4$	$a = 14.493 \text{ \AA}$	31
$\text{NdBa}_2\text{CuO}_7$	Pmmm; $a = 3.878$, $b = 3.913$, $c = 11.753 \text{ \AA}$	58

BRIEF ATTACHMENT AD

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

Date: March 14, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

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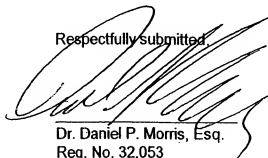
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ATTACHMENT AD

THEORY OF SUPERCONDUCTIVITY

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Fundamental Facts

(a) Superconductivity was discovered in 1911 by Kamerlingh-Onnes.¹ He was the first to liquefy helium and so to produce temperatures below 10° K. With this new technique he was able to observe the continued decrease of the electrical resistance of metals with decreasing temperature. With mercury, in contrast to other metals, he was astonished to find that the resistance completely vanished, almost discontinuously, at about 4.2° K (Fig. 1-1). Today superconductivity is known in 18 other metals (see Table 1-1) whereas in others, e. g., gold and bismuth, the conductivity remains normal far below even 1° K. Many alloys and compounds can also become superconducting, in particular the frequently used niobium nitride which has a transition temperature as high as 20° K. However, among these latter substances hysteresis phenomena mentioned in the "Introduction" are so much more strongly evident that in testing the present theory we prefer to employ only the "good" superconductors, i. e., the pure elements.

In the ideal case the resistance vanishes completely and discontinuously at a transition temperature T_s . Actually the resistance-temperature curve does fall more sharply the more the specimen is like a single crystal and the smaller the measuring current used. Because the drop always occurs in a measurable temperature range, the experimental definition of the transition temperature is to some extent arbitrary. The temperature at

which the direct-current resistance reaches one half of the value it had just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

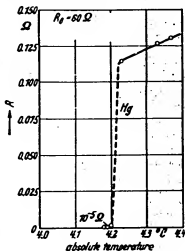


Fig. 1-1. Appearance of superconductivity in mercury according to H. Kamerlingh-Onnes (1911). The ordinate is the resistance R ; R_0 the resistance of solid mercury extrapolated to 0° C, is 60 ohms.

¹H. Kamerlingh-Onnes, *Commun. Leiden*, 120b, 122b, 124c, (1911).

BRIEF ATTACHMENT AE

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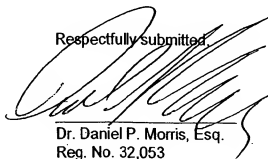
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(24) New superconductive compounds of the K2NIF4 structural type having a high transition temperature, and method for fabricating same.

(27) The superconductive compounds are oxides of the general formula $RE_{2-x}AE_yTM.O_{4-y}$, wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two member of that group, and TM is a transition metal, and wherein $x < 0.3$ and $0.1 \leq y \leq 0.5$. The method for making these compounds involves the steps of coprecipitating aqueous solutions of the respective nitrates of the constituents and adding the coprecipitate to oxalic acid, decomposing the precipitate and causing a solid-state reaction at a temperature between 500 and 1200°C for between one and eight hours, forming pellets of the powdered product at high pressure, sintering the pellets at a temperature between 500 and 1000°C for between one half and three hours, and subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for between one half and five hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product.

EP 0 275 343 A1

NEW SUPERCONDUCTIVE COMPOUNDS OF THE K-NiF₄ STRUCTURAL TYPE HAVING A HIGH TRANSITION TEMPERATURE, AND METHOD FOR FABRICATING SAME

Field of the Invention

The invention relates to a new class of superconductors, in particular to compounds of the K₂NiF₄ type of structure having superconductor properties below a relatively high transition temperature, and to a method for manufacturing those compounds.

Background of the Invention

Superconductivity is usually defined as the complete loss of electrical resistance of a material at a well-defined temperature. It is known to occur in many materials: About a quarter of the elements and over 1000 alloys and compounds have been found to be superconductors. Superconductivity is considered a property of the metallic state of the material, in that all known superconductors are metallic under the conditions that cause them to superconduct. A few normally non-metallic materials, for example, become superconductive under very high pressure, the pressure converting them to metals before they become superconductors.

Superconductors are very attractive for the generation and energy-saving transport of electrical power over long distances, as materials for forming the coils of strong magnets for use in plasma and nuclear physics, in nuclear resonance medical diagnosis, and in connection with the magnetic levitation of fast trains. Power generation by thermonuclear fusion, for example, will require very large magnetic fields which can only be provided by superconducting magnets. Certainly, superconductors will also find application in computers and high-speed signal processing and data communication.

While the advantages of superconductors are quite obvious, the common disadvantage of all superconductive materials so far known lies in their very low transition temperature (usually called the critical temperature T_c) which is typically on the order of a few degrees Kelvin. The element with the highest T_c is niobium (9.2 K), and the highest known T_c is about 23 K for Nb₃Ge at ambient pressure.

Accordingly, most known superconductors require liquid helium for cooling and this, in turn, requires an elaborate technology and as a matter of principle involves a considerable investment in cost and energy.

It is, therefore, an object of the present inven-

tion to propose compositions for high- T_c superconductors and a manufacturing method for producing compounds which exhibit such a high critical temperature that cooling with liquid helium is obviated so as to considerably reduce the cost involved and to save energy.

The present invention proposes to use compounds having a layer-type structure of the kind known from potassium nickel fluoride K₂NiF₄. This structure is in particular present in oxides of the general composition RE₂TM₂O₈, wherein RE stands for the rare earths (lanthanides) and TM stands for the so-called transition metals. It is a characteristic of the present invention that in the compounds in question the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline earth group, and that the oxygen content is at a deficit.

For example, one such compound that meets the description given above is lanthanum copper oxide La₂CuO₄ in which the lanthanum - which belongs to the IIIB group of elements - is in part substituted by one member of the neighboring IIA group of elements, viz. by one of the alkaline earth metals (or by a combination of the members of the IIA group), e.g., by barium. Also, the oxygen content of the compound is incomplete such that the compound will have the general composition La_{2-x}Ba_xCuO_{4-y}, wherein $x \leq 0.3$ and $y < 0.5$.

Another example for a compound meeting the general formula given above is lanthanum nickel oxide wherein the lanthanum is partially substituted by strontium, yielding the general formula La_{2-x}Sr_xNiO_{4-y}. Still another example is cerium nickel oxide wherein the cerium is partially substituted by calcium, resulting in Ce_{2-x}Ca_xNiO_{4-y}.

The following description will mainly refer to barium as a partial replacement for the lanthanum in a La₂CuO₄ compound because it is the Ba-La-Cu-O system which is, at least at present, the best understood system of all possible. Some compounds of the Ba-La-Cu-O system have been described by C. Michel and B. Raveau in Rev. Chim. Min. 21 (1984) 407, and by C. Michel, L. Er-Rakho and B. Raveau in Mat. Res. Bull., Vol. 20, (1985) 667-671. They did, however, not find nor try to find, superconductivity.

Experiments conducted in connection with the present invention have revealed that high- T_c superconductivity is present in compounds where the rare earth is partially replaced by any one or more of the other members of the same IIA group of elements, i.e. the other alkaline earth metals. Ac-

tually, the T_c of $\text{La}_2\text{CuO}_{4-y}$ with Sr^{2+} is higher and is superconductivity-induced diamagnetism larger than that found with Ba^{2+} and Ca^{2+} .

As a matter of fact, only a small number of oxides is known to exhibit superconductivity, among them the Li-Ti-O system with onsets of superconductivity as high as 13.7 K, as reported by D.C. Johnston, H. Prakash, W.H. Zachariasen and R. Visvanathan in *Mat. Res. Bull.* 8 (1973) 777. Other known superconductive oxides include Nd-doped SrTiO_3 and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, reported respectively by A. Baraloff and G. Binnig in *Physics* 108B (1981) 1335, and by A.W. Sleight, J.L. Gillson and F.E. Bierstedt in *Solid State Commun.* 17 (1975) 27.

The X-ray analysis conducted by Johnston et al. revealed the presence in their Li-Ti-O system of three different crystallographic phases, one of them, with a spinel structure, showing the high critical temperature. The Ba-La-Cu-O system, too, exhibits a number of crystallographic phases, namely with mixed-valent copper constituents which have itinerant electronic states between non-Jahn-Teller Cu^{3+} and Jahn-Teller Cu^{2+} ions.

This applies likewise to systems where nickel is used in place of copper, with Ni^{3+} being the Jahn-Teller constituent, and Ni^{2+} being the non-Jahn-Teller constituent.

The existence of Jahn-Teller polarons is conducting crystals was postulated theoretically by K.H. Hoek, H. Nickisch and H. Thomas in *Helv. Phys. Acta* 56 (1983) 237. Polarons have large electron-phonon interactions and, therefore, are favorable to the occurrence of superconductivity at high critical temperatures.

Generally, the Ba-La-Cu-O system, when subjected to X-ray analysis reveals three individual crystallographic phases, viz.

- a first layer-type perovskite-like phase, related to the K_2NiF_4 structure, with the general composition $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$, with $x < 1$ and $y > 0$;
- a second, non-conducting CuO phase; and
- a third, nearly cubic perovskite phase of the general composition $\text{La}_{1-x}\text{Ba}_x\text{CuO}_3$ which appears to be independent of the exact starting composition,

as has been reported in the paper by J.G. Bednorz and K.A. Müller in *Z. Phys. B - Condensed Matter* 64 (1986) 189-193. Of these three phases the first one appears to be responsible for the high- T_c superconductivity, the critical temperature showing a dependence on the barium concentration in that phase. Obviously, the Ba^{2+} substitution causes a mixed-valent state of Cu^{2+} and Cu^{3+} to preserve charge neutrality. It is assumed that the oxygen deficiency, y , is the same in the doped and undoped crystallites.

Both La_2CuO_4 and LaCuO_3 are metallic conduc-

tors at high temperatures in the absence of barium. Actually, both are metals like LaNiO_3 . Despite their metallic character, the Ba-La-Cu-O type materials are ceramics, as are the other compounds of the $\text{RE}_2\text{TM}_2\text{O}_4$ type, and their manufacture more or less follows the known principles of ceramic fabrication. The preparation of a Ba-La-Cu-O compound, for example, in accordance with the present invention typically involves the following manufacturing steps:

- Preparing aqueous solutions of the respective nitrates of barium, lanthanum and copper and coprecipitation thereof in their appropriate ratios.
- Adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates.
- Decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for one to eight hours.
- Pressing the resulting product at a pressure of about 4 kbar to form pellets.
- Re-heating the pellets to a temperature between 500 and 900°C for one half to three hours for sintering.

It will be evident to those skilled in the art that if the partial substitution of the lanthanum by strontium or calcium is desired, the particular nitrate thereof will have to be used in place of the barium nitrate of the example described above. Also, if the copper of this example is to be replaced by another transition metal, the nitrate thereof will obviously have to be employed.

Experiments have shown that the partial contents of the individual compounds in the starting composition play an important role in the formation of the phases present in the final product. While, as mentioned above, the final Ba-La-Cu-O system obtained generally contains the said three phases, with the second phase being present only to a very small amount, the partial substitution of lanthanum by strontium or calcium (and perhaps beryllium) will result in only one phase existing in the final $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ or $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$, respectively, provided $x < 0.3$.

With a ratio of 1:1 for the respective (Ba, La) and Cu contents, one may expect the said three phases to occur in the final product. Setting aside the said second phase, i.e. the CuO phase, whose amount is negligible, the relative volume amounts of the other two phases are dependent on the barium contents in the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ complex. At the 1:1 ratio and with an $x = 0.02$, the onset of a localization transition is observed, i.e. the resistivity increases with decreasing temperature, and there is no superconductivity.

With $x = 0.1$ at the same 1:1 ratio, there is a resistivity drop at the very high critical temperature of 35 K.

With a (Ba,Lu) versus Cu ratio of 2:1 in the starting composition, the composition of the $\text{La}_2\text{CuO}_4\text{Ba}$ phase, which was assumed to be responsible for the superconductivity, is imitated, with the result that now only two phases are present, the CuO phase not existing. With a barium content of $x = 0.15$, the resistivity drop occurs at $T_c = 26$ K.

The method for preparing the Ba-La-Cu-O complex involves two heat treatments for the precipitate at an elevated temperature for several hours. In the experiments carried out in connection with the present invention it was found that best results were obtained at 900°C for a decomposition and reaction period of 5 hours, and again at 900°C for a sintering period of one hour. These values apply to a ratio 1:1 composition as well as to a 2:1 composition.

For the ratio 2:1 composition, a somewhat higher temperature is permissible owing to the melting point of the composition being higher in the absence of excess copper oxide. Yet it is not possible by high-temperature treatment to obtain a one-phase compound.

Measurements of the dc conductivity were conducted between 300 and 4.2 K. For barium-doped samples, for example, with $x < 0.3$, at current densities of 0.5 A/cm^2 , a high-temperature metallic behavior with an increase in resistivity at low temperatures was found. At still lower temperatures, a sharp drop in resistivity (>90%) occurred which for higher current densities became partially suppressed. This characteristic drop was studied as a function of the annealing conditions, i.e. temperature and oxygen partial pressure. For samples annealed in air, the transition from itinerant to localized behavior was not found to be very pronounced, annealing in a slightly reducing atmosphere, however, led to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop was shifted towards higher values of the critical temperature. Longer annealing times, however, completely destroy the superconductivity.

Cooling the samples from room temperature, the resistivity data first show a metal-like decrease. At low temperatures, a change to an increase occurs in the case of Ca compounds and for the Ba-substituted samples. This increase is followed by a resistivity drop, showing the onset of superconductivity at 22 ± 2 K and 33 ± 2 K for the Ca and Ba compounds, respectively. In the Sr compound, the resistivity remains metallic down to the resistivity drop at 40 ± 1 K. The presence of localization effects, however, depends strongly on alkaline-earth ion concentration and sample preparation, that is to say, annealing conditions and also on the density which have to be optimized. All samples with low

concentrations of Ca, Sr, and Ba show a strong tendency to localization before the resistivity drop occurs.

Apparently, the onset of the superconductivity, i.e. the value of the critical temperature T_c , is dependent, among other parameters, on the oxygen content of the final compound. It seems that a certain oxygen deficiency is necessary for the material to have a high- T_c behavior. In accordance with the present invention, the method described above for making the $\text{La}_2\text{CuO}_4\text{Ba}$ complex is complemented by an annealing step during which the oxygen content of the final product can be adjusted. Of course, what was said in connection with the formation of the $\text{La}_2\text{CuO}_4\text{Ba}$ compound, likewise applies to other compounds of the general formula $\text{RE}_2\text{TM}_2\text{O}_{4-x}\text{AE}$, such as, e.g. $\text{Nd}_2\text{NiO}_4\text{Sr}$.

In the cases where a heat treatment for decomposition and reaction and/or for sintering was performed at a relatively low temperature, i.e. at no more than 950°C , the final product is subjected to an annealing step at about 900°C for about one hour in a reducing atmosphere. It is assumed that the net effect of this annealing step is a removal of oxygen atoms from certain locations in the matrix of the $\text{RE}_2\text{TM}_2\text{O}_4$ complex, thus creating a distortion in its crystalline structure. The O_2 partial pressure for annealing in this case may be between 10^1 and 10^5 bar.

In those cases where a relatively high temperature (i.e. above 950°C) was employed for the heat treatment, it might be advantageous to perform the annealing step in a slightly oxidizing atmosphere. This would make up for an assumed exaggerated removal of oxygen atoms from the system owing to the high temperature and resulting in a too severe distortion of the system's crystalline structure.

Resistivity and susceptibility measurements, as a function of temperature, of Sr^{2+} and Ca^{2+} -doped $\text{La}_2\text{CuO}_{4-x}$ ceramics show the same general tendency as the Ba^{2+} -doped samples: A drop in resistivity $\rho(T)$, and a crossover to diamagnetism at a slightly lower temperature. The samples containing Sr^{2+} actually yielded a higher onset than those containing Ba^{2+} and Ca^{2+} . Furthermore, the diamagnetic susceptibility is about three times as large as for the Ba samples. As the ionic radius of Sr^{2+} nearly matches the one of La^{3+} , it seems that the size effect does not cause the occurrence of superconductivity. On the contrary, it is rather adverse, as the data on Ba^{2+} and Ca^{2+} indicate.

The highest T_c 's for each of the dopant ions investigated occur for those concentrations where, at room temperature, the $\text{RE}_2\text{TM}_2\text{O}_{4-x}$ structure is close to the orthorhombic-tetragonal structural phase transition which may be related to the substantial electron-phonon interaction enhanced by the substitution. The alkaline-earth substitution of

the rare earth metal is clearly important, and quite likely creates TM ions with no e_g Jahn-Teller orbitals. Therefore, the absence of these J-T. orbitals, that is, J-T. holes near the Fermi energy probably plays an important role for the T_c enhancement.

Claims

1) Superconductive compound of the $RE_2TM.O_x$ type having a transition temperature above 28 K, wherein the rare earth (RE) is partially substituted by one or more members of the alkaline earth groups of elements (AE), and wherein the oxygen content is adjusted such that the resulting crystal structure is distorted and comprises a phase of the general composition $RE_{2-x}AE_xTM.O_{x+y}$, wherein TM represents a transition metal, and $x < 0.3$ and $y < 0.5$.

2) Compound in accordance with claim 1, wherein the rare earth (RE) is lanthanum and the transition metal (TM) is copper.

3) Compound in accordance with claim 1, wherein the rare earth is cerium and the transition metal is nickel.

4) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is nickel.

5) Compound in accordance with claim 1, wherein barium is used as a partial substitute for the rare earth, with $x < 0.3$ and $0.1 \leq y \leq 0.5$.

6) Compound in accordance with claim 1, wherein calcium is used as a partial substitute for the rare earth, with $x < 0.3$ and $0.1 \leq y \leq 0.5$.

7) Compound in accordance with claim 1, wherein strontium is used as a partial substitute for the rare earth, with $x < 0.3$ and $0.1 \leq y \leq 0.5$.

8) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is chromium.

9) Compound in accordance with claim 1, wherein the rare earth is neodymium and the transition metal is copper.

10) Method for making superconductive compounds of the $RE_2TM.O_x$ type, with RE being a rare earth, TM being a transition metal, the compounds having a transition temperature above 28 K, comprising the steps of:

- preparing aqueous solutions of the nitrates of the rare earth and transition metal constituents and of one or more of the alkaline earth metals and coprecipitation thereof in their appropriate ratios;
- adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates;
- decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for a period of

time between one and eight hours;

- allowing the resultant powder product to cool;
- pressing the powder at a pressure of between 2 and 10 kbar to form pellets;

5 - re-adjusting the temperature of the pellets to a value between 500 and 1000°C for a period of time between one half and three hours for sintering;

10 - subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for a period of time between one half and 5 hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product which has a final composition of the form $RE_2TM.O_{x+y}$, wherein $x < 0.3$ and $0.1 < y < 0.5$.

11) Method in accordance with claim 10, wherein the protected atmosphere is pure oxygen.

12) Method in accordance with claim 10, wherein the protected atmosphere is a reducing atmosphere with an oxygen partial pressure between 10^{-1} and 10^{-5} bar.

13) Method in accordance with claim 10, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed at a temperature of 900°C for one hour in a reducing atmosphere with an oxygen partial pressure between 10^{-1} and 10^{-5} bar.

14) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with $x < 0.2$, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of 10^{-3} bar and at a temperature of 900°C for one hour.

15) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with $x < 0.2$, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of 10^{-3} bar and at a temperature of 900°C for one hour.

16) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein calcium is used to partially substitute for the lanthanum, with $x < 0.2$, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of 10^{-3} bar and at a temperature of 900°C for one hour.

17) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein strontium is used to partially substitute for the lanthanum, with $x < 0.2$, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of 10^{-3} bar and at a temperature of 900°C for one hour.

18) Method in accordance with claim 10, wherein cerium is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the cerium, with $x < 0.2$, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of 10^{-3} bar and at a temperature of 900°C for one hour.

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BRIEF ATTACHMENT AF

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

Date: March 14, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

**For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION**

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

THIRD SUPPLEMENTAL AMENDMENT

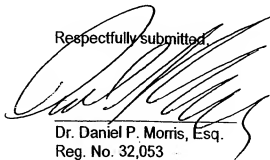
Sir:

In response to the Office Action dated July 28, 2004, please consider the following:

The attachments referred to herein A to Z and AA are in the FIRST SUPPLEMENTAL AMENDMENT. The Attachments AB to AG are attached herein.

Please charge any fee necessary to enter this paper and any previous paper to deposit account 09-0468.

Respectfully submitted,



Dr. Daniel P. Morris, Esq.
Reg. No. 32,053
(914) 945-3217

IBM CORPORATION
Intellectual Property Law Dept.
P.O. Box 218
Yorktown Heights, New York 10598

ATTACHMENT AF

COPPER OXIDE SUPERCONDUCTORS

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with help from

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C. R. Sanders

*Department of Physics and Astronomy
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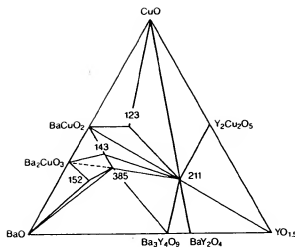
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S39.6 '23-dc 19 88-18569 CIP
ISBN 0-471-62342-3

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G2



Compound	Slowly cooled to room temperature
123 - $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$	O_7
143 - $\text{YBa}_4\text{Cu}_3\text{O}_{8.5+\delta}$	O_9
385 - $\text{Y}_3\text{Ba}_8\text{Cu}_5\text{O}_{17.5+\delta}$	O_{18}
152 - $\text{YBa}_2\text{Cu}_2\text{O}_{8.5+\delta}$	O_9
211 - Y_2BaCuO_5	
$\text{Ba}_2\text{CuO}_3+\delta$	$\text{O}_{3.3}$

Fig. V-2. Ternary phase diagram of the Y_2O_3 -BaO-CuO system at 950°C . The green phase [Y_2BaCuO_5 , (211)] the superconducting phase [$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, (123)], and three other compounds are shown in the interior of the diagram (DeLee).

B. METHODS OF PREPARATION

In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical processes involved in the transformation of a mixture of compounds into a superconductor. The coprecipitation technique mixes the constituents on an atomic scale and forms fine powders, but it requires careful control of the pH and some familiarity with analytical chemistry. The sol-gel procedure requires more competence in analytical procedures.

In the solid-state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates, or carbonates of Ba, Bi, La, Sr, Tl, Y, or other elements. Sometimes nitrates are formed first by dissolving oxides in nitric acid and decomposing the solution at 500°C before calcination

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(e.g., Davis, Holla, Kelle). These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcining for an extended period (≈ 20 hr) at elevated temperatures ($\approx 900^\circ\text{C}$). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step. As the reaction proceeds, the color of the charge changes. The process usually ends with a final oxygen anneal followed by a slow cool down to room temperature of the powder, or pellets made from the powder, by sintering in a cold or hot press. Sintering is not essential for the chemical process, but for transport and other measurements it is convenient to have the material pelletized. A number of researchers have provided information on this solid-state reaction approach (e.g., Allge, Finez, Galla, Garla, Gopal, Gubse, Hajk1, Hatan, Herm, Hika1, Hirab, Jayar, Maen1, Mood1, Mood2, Neume, Poepp, Polle, Qadri, Rhyne, Ruzic, Saito, Sait1, Sawa1, Shamo, Takit, Tothz, Wuzz3).

Some of the earlier works on foils, thick films, wires, or coatings employed a suspension of the calcined powder in a suitable organic binder, and the desired product was obtained by conventional industrial processes such as extruding, spraying, or coating.

In the second or coprecipitation process the starting materials for calcination are produced by precipitating them together from solution (e.g., Asela, Bedno, Leez7, Wang2). This has the advantage of mixing the constituents on an atomic scale. In addition the precipitates may form fine powders whose uniformity can be controlled, which can eliminate some of the labor. Once the precipitate has been dried, calcining can begin as in the solid-state reaction procedure. A disadvantage of this method, at least as far as the average physicist or materials scientist is concerned, is that it requires considerable skill in chemical procedures.

Another procedure for obtaining the start-up powder is the sol-gel technique in which an aqueous solution containing the proper ratios of Ba, Cu, and Y nitrates is emulsified in an organic phase and the resulting droplets are gelled by the addition of a high-molecular-weight primary amine which extracts the nitric acid. This process was initially applied to the La materials, but has been perfected for YBaCuO as well (Cimaz, Hatfi).

When using commercial chemical supplies to facilitate the calcination process a dry or wet (acetone) pregrinding with an agate mortar and pestle or a ball mill is recommended. Gravimetric amounts of the powdered precursor materials are thoroughly mixed and placed in a platinum or ceramic crucible. Care must be taken to ensure the compatibility of the ceramic crucible with the chemicals to obviate reaction and corrosion problems.

Complete recipes for the YBa material have been described (e.g., Gran2). Typically, the mixture of unreacted oxides is calcined in air or oxygen around 900°C for 15 hr. During this time the YBaCuO mixture changes color from the green Y_2BaCuO_5 phase to the dark gray $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound. Then the charge is taken out, crushed, and scanned with X rays to determine its purity. If warranted by the powder pattern X-ray scan, the calcination process is repeated. Often, at this stage the material is very oxygen poor, and electrically it is semi-

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conducting or even nonconducting. After pelletizing at $>10^5$ psi the pellet is sintered for several hours at $\approx 900^\circ\text{C}$ in flowing oxygen and then slowly cooled at $\approx 3^\circ\text{C}/\text{min}$ down to room temperature. Slow cooling from the elevated temperature is important for producing the low-temperature orthorhombic superconductor phase. The tetragonal nonsuperconducting phase may be obtained by quenching. The pellet may be used as is or it may be cut into suitable sizes by sand blasting, with a diamond saw, or with an arc. After vigorous machining another oxygen anneal (450°C , 1 hr, slow cool down) is often required to preserve the superconducting properties.

An example of preparing a Bi-based superconductor involves mixing gravimetric amounts of high-purity Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO powders, calcining them in air at 750 – 890°C , regrounding them, and then repeating these procedures several times. Then pellets of the calcined product were sintered at the same temperature and quenched to room temperature (Chuz5). Figure V-1 shows the effect of sample treatment on the resistance versus temperature curve.

WARNING: As was mentioned above, thallium is a toxic material and proper precautions must be taken when working with it. It is useful to start by preparing the high-quality precursor compound BaCu_3O_4 or $\text{Ba}_2\text{Cu}_3\text{O}_5$ by reacting the oxides in air at 925°C for 24 hr. Then appropriate amounts of Tl_2O_3 are added, powdered, and pelletized. The pellet is then heated to 880 – 910°C for a few minutes in flowing oxygen, and at the onset of melting it is quenched to room temperature (Shen1).

Allan Hermann has suggested consulting the following references for information on thallium poisoning and antidotes thereto: H. Heydlauf, *Euro. J. Pharmacol.* 6, 340 (1969), which discusses thallium poisoning and describes the antidote ferric cyanoferrate, and *Int. J. Pharmacol.* 10, 1 (1974), which discusses cases of thallium intoxication treated with Prussian Blue.

C. ADDITIONAL COMMENTS ON PREPARATION

This section will treat some additional methods which have been employed for the preparation of samples.

In one experiment coprecipitated nitrates of La, Sr, Cu, and Na carbonate were calcined for 2 hr at 825°C , pressed into pellets, and then subjected to shock compression of ≈ 20 GPa at an estimated peak temperature of $\approx 1000^\circ\text{C}$ (Graha). The best superconductivity was observed after 1 hr of air exposure at 1100°C . Shock compression fabrication has also been reported (Murrz, Murr1) for YBa_2 and other rare-earth derivatives. This process produced "monoliths," distinct from the usual composites.

Another technique involved the formation of a precursor alloy of Eu, Ba, Cu or Yb, Ba, Cu by rapid solidification, with the superconducting materials obtained subsequently by oxidation (Halda). A novel method involved preparing

the superconductors from molten Ba-Cu oxides and solid rare-earth-containing materials. In principle this process may be better controlled and complicated shapes can be molded or cast (Herma).

Pulsed current densities of $300\text{--}400\text{ Å/cm}^2$ with rise times of $0.6\text{ }\mu\text{sec}$ at room temperature were used to convert the weakly semiconducting phase of YBaCuO to the stable metallic phase (Djure, Djuri).

A claim was made that thermal cycling from cryogenic temperatures to 240 K raised the T_c of YBa_x and YBaCuO-F (with some F substituting for O) to 159 K. Cycling above 140 K lowered T_c . This cycling process could possibly change the density of twins and thereby enhance T_c .

A freeze-drying technique was reported as producing sintered materials homogeneous in composition and small in porosity (Stras). The low-temperature firing of oxalates ($T < 780^\circ\text{C}$) has also been reported as producing a homogeneous material of small grain size (Manth).

Both Bi and Pb act as fluxes during the sintering process (Kilco). Bismuth substitution appears to reduce the normal state resistivity by about an order of magnitude without affecting the superconducting properties.

A convenient method of separating the superconducting particles from a powdered mixture using magnetic levitation has been reported (Barso). This may be used to select the superconducting fraction after each calcination process.

D. FILMS

The new ceramic oxide superconductors presently lack mechanical properties such as ductility which are needed for high-current applications like magnet wire fabrication (Jinzz-Jinz3) and power transmission. To circumvent some of these deficiencies for microelectronic applications one can prepare thin films on suitable substrates. Some devices such as Josephson junctions require thin superconducting films. Many workers have discussed the preparation and properties of LaSrCuO (e.g., Adach, Delim, Kaws, Koinu, Matsu, Nagat, Naito, Tera1) and YBaCuO (e.g., Burbi, Charz, Evett, Gurvi, Hause, Hongz, Inamz, Kwozz, Kwozi, Manki, Scheu, Somek, Wuzz4) type films.

Almost every conceivable thin-film deposition technique such as electron beam evaporation, molecular beam epitaxy, sputtering, magnetron, laser ablation, screening, and spraying has been tried with the copper oxide system. Some of these techniques require expensive, elaborate apparatus, although descriptions of simple thin-film deposition systems are also available (e.g., see Koin1). Some representative examples of deposition procedures will be discussed.

Epitaxial films of $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ on (100) SrTiO_3 were produced using three separate electron beam sources (e.g., Chaud, Chau1, Laibo). The deposition was done in $10^{-4}\text{--}10^{-3}$ torr O_2 with a substrate temperature of 400°C . The deposited films were atomically amorphous with a broad X-ray peak. The epitaxial ordering was achieved upon annealing in O_2 at 900°C with the orthorhombic c axis essentially perpendicular to the plane.

High-quality beam to evaporator (Hammo, C) ited film in oxyg 750°C for 1 hr, furnace.

Superconducting range (Ma) was Ar or an Ar 10^{-7} torr and, v $\text{ZrO}_2\text{--}9\%$ Y_2O_3 films. The films: gen annealing. : erties dependec conditions, con

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High-quality superconducting films were obtained using a multiple electron beam to evaporate metallic sources in a flow of molecular oxygen at 4.5×10^{-6} torr (Hammo, Ohzzz). The deposition rate was 10 \AA/sec . To anneal the deposited film in oxygen it was heated for 3-6 hr in a flow of oxygen at 650°C , raised to 750°C for 1 hr, then to 850°C for 1 hr, and finally slowly cooled down in the furnace.

Superconducting films were prepared using a double ion beam sputtering arrangement (Madak). The target beam was Ar at 40 mA, and the substrate beam was Ar or an Ar-O₂ mixture at 10-500 eV and 2 mA. The base pressure was 5×10^{-7} torr and, with the gas, 4×10^{-4} torr. The best substrate materials such as ZrO₂-9% Y₂O₃ did not appreciably interact, diffuse, or change the deposited films. The films were $\approx 1 \mu\text{m}$ thick and were rendered superconducting by oxygen annealing. Zero resistance was attained at 88 K. The superconducting properties depended upon the ion beam energy, substrate temperature, annealing conditions, composition, and the extent of poisoning from the substrate.

Films of dysprosium barium copper oxide were grown (Webbz) by molecular beam epitaxy (MBE) using a Varian 360 MBE system, and the nucleation process was monitored by reflection high-energy electron diffraction (RHEED). The copper was incompletely oxidized in metallic microcrystals growing in a sea of amorphous Ba and Dy. After deposition superconducting films were obtained by high-temperature oxygen annealing.

Films of Y_{1.1}Ba_{1.3}Cu₃O_{6.4} approximately 3300 \AA thick with a surface roughness of 500 \AA were prepared (Dijkk, Inamz, Wuzz4). These films were deposited on SrTiO₃, sapphire, and vitron carbon by evaporation from a single bulk pellet of YBaCuO 1 cm diameter and 0.2 cm thick at a pressure of 5×10^{-7} torr. The evaporation was produced by several thousand pulses of laser irradiation (3-6 Hz, $\approx 30 \text{ nsec}$ width, 1 J/pulse, 2 J/cm²). For best results the substrate was heated to 450°C . As deposited thin films were well bonded to the substrate and they appeared shiny dark brown and were electrically insulating. The films were oxygen annealed at 900°C for 1 hr and then slowly cooled over a period of several hours. Standard four-probe resistivity measurements indicated the onset of superconductivity around 95 K and, for a (100) SrTiO₃ substrate, with zero resistivity achieved near 85 K. The laser ablation technique was also employed for LaSr_x (Moorj) and YBa_x (Naral).

Films were obtained from sandwiched multilayers by depositing Y₂O₃, BaO, and Cu in layers (Nasta, Tsaur) on ZrO₂, MgO, and sapphire substrates at 200°C and 10^{-5} torr. Oxygen treatment for 1-2 hr at $\approx 850^\circ\text{C}$ permitted the layers to diffuse, homogenize, and oxygenate, and thereby form the superconducting compound (Baosz). Films on Ni have also been reported in which superconductivity was obtained by a diffusion process involving the Cu substrate, Y₂O₃, and BaCO₃ composite (Tachi).

Some 5000- \AA thick films of YBaCuO have been deposited using an ultrahigh vacuum dc-magnetron getter-sputter deposition system. The deposition rate was 0.2 \AA/sec , the substrate temperature was 1050°C , and the target-to-substrate distance was 12 cm. The scattering was done in an Ar-O₂ atmosphere.

The X-ray and electron microscope examinations indicated some variation among the substrates arranged on the heater. Inhomogeneities were observed even within the film made on a single substrate. As deposited the films were oxygen deficient, and annealing produced suitable compositions. The reversible oxygen incorporation was monitored by the systematic splitting of the strongest X-ray peaks. The oxygen diffusion coefficient at 600°C was 10^{-15} m²/sec and the activation energies for desorption and absorption were 1.1 and 1.7 eV, respectively. The highest onset temperature was 99 K with complete superconduction at 40 K. Exposure to water inhibited the superconductor (Barns, Kishi, Yanzz). A device structure with a Y₂O₃ barrier has also been studied (Blami).

Another work showed that films produced by dc magnetron sputtering are copper deficient if the substrate-to-target distance is large or if the substrate is at an elevated temperature (Leez5).

Superconducting YBaCuO thin films with a large surface area (≈ 5 cm \times 5 cm) were grown on Al₂O₃, sapphire, and MgO up to a 500°C substrate temperature by magnetron and diode techniques. Rutherford back scattering (RBS) indicated a uniform composition across magnetron-deposited film areas with diameters up to 5 cm, and the diode film composition homogeneity was even better, but over a smaller area (≈ 2.5 cm diameter). The as-deposited films were annealed in oxygen at different temperatures and exposure times. Prolonged high-temperature annealing ($> 850^\circ\text{C}$) increased the impurity phase. The highest T_c films had a wide range of composition, with the maximum T_c film copper rich. On the basis of an in-situ resistivity study of YBa* thin films a rapid heating to about 900°C in flowing helium followed by slow cool down in flowing oxygen was recommended (David).

The post-deposition anneal cycle was avoided by producing the films in a high-pressure reactive evaporation process involving rapid thermal annealing (Lathr). Smooth films were obtained on zirconia and SrTiO₃ substrates. Screen printing of oxide superconducting films is also possible (Budha, Fuzz1), and simple spray deposition has been reported (Gupta). Films have also been made by coating and spinning off the solutions. Aqueous and aqueous-alcoholic mixed solutions of the metal nitrates (Coop2), metal acetates in dilute acetic acid (Rice1), and sol-gels (Kram1) have all been reported. These processes are potentially important for commercial superconducting coatings on silicon (Kram1), on yttrium-stabilized zirconia (YSZ), on SrTiO₃ (Coop2, Gupta), and on MgO (Gupta, Rice1).

E. SINGLE CRYSTALS

The bulk properties of oxide superconductors are averages over components parallel and perpendicular to the Cu-O planes. In addition, for orthorhombic samples there is an averaging over properties that differ for the *a* and *b* directions in this plane. This in-plane anisotropy is especially pronounced for the YBa* 123 structure in which the Cu-O-Cu chains lie along the *b* axis. The

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F. ALIGNI

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best way to understand these materials is through experiments on perfect single crystals. Unfortunately, untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals are not available so the a, b anisotropy cannot be resolved. Tetragonal superconductors should not have this twinning problem. In this work twinned monocrystals will be referred to as single crystals.

A number of experiments have been carried out on monocrystals such as X-ray diffraction (e.g., Borde, Hazen, Lepag, Siegr, Onoda), magnetic studies (e.g., Crabt, Schnl, Worth), mechanical measurements (e.g., Cookz, Dinge), and micro-Raman spectroscopy (e.g., Hemle). In this section we will briefly describe how such crystals are made. The December 1987 issue of the *Journal of Crystal Growth* was devoted to superconductors.

Millimeter-size $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ single crystals were grown in a molten copper oxide flux (Kawal). Another basic technique employs other fluxes (Haned, Taka4, Zhou1), namely, PbF_2 , B_2O_3 , PbO , PbO_2 , with the risk of possible Pb contamination. LaSr_2 crystals were also grown by the solid phase reaction using a hot press of pellets (Iwazu) and rapid quenching of a nonstoichiometric melt (Satoz).

Small single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ have been prepared from a sintered powder which was formed into a pellet and then heated, first in a reducing atmosphere and then in an oxidizing one at 925°C . Annealing a stoichiometric mixture also produced monocrystals (Liuzz). Millimeter-size crystals were grown by melting a stoichiometric mixture of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ plus excess CuO at 1150°C followed by holding at 900°C for 4 days (Damen, see also Fine1).

A gold crucible on a gold or alumina sheet was used to obtain free-standing ($1 \times 2 \times 0.1 \text{ mm}$) single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Kaise, Kais1, Holtz). A charge of 2 g was heated in air at $200^\circ\text{C}/\text{hr}$ and held at 975°C for 1.5 hr, then it was cooled to 400°C at $25^\circ\text{C}/\text{hr}$. The molten charge creeps and forms single crystals and twins on the surfaces. The larger crystals formed in the space between the bottom of the crucible and the gold support sheet.

A detailed account has appeared of the preparation of a 123 compound single crystal by the flux method (Zhou1). The flux mole ratio $\text{BaO}_2:\text{CuO}$ was between 1:3 and 2:5, and the nutrient $\text{Y}_2\text{O}_3:\text{BaO}_2:\text{CuO}$ mole ratios were 0.5:2:3. A multistep temperature process was employed. Black single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were found at the bottom and at the edge between the wall and the bottom of the crucibles. Platinum crucibles seemed to contaminate the samples so alumina crucibles were recommended. Crystals as large as $2 \times 2 \times 0.3 \text{ mm}^3$ were reported. A similar technique was used to produce single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{DyBa}_2\text{Cu}_3\text{O}_{7-x}$ as large as 4 mm (Schn1).

F. ALIGNED GRAINS

Clearly high-quality single crystals are important for understanding the physics of superconductors. However, much useful information about anisotropies can

be obtained by studying the properties of aligned grains, which are much easier to fabricate.

A superconducting sample can be initially a collection of randomly oriented grains, but various techniques can be used to partially orient these grains so that the *c* axis lies preferentially in a particular direction. For example uniaxial compression tends to orient compacted grains, with compressed 90- μm particles exhibiting more alignment than compressed 10- μm particles (Glowa). Epoxy-embedded grains have been aligned under the influence of an applied magnetic field and pressure (Arend).

X-ray and magnetic measurements have been reported on aligned crystalline grains of YBa_x (Farr1). Optical studies have also been made on aligned grains. The critical current density for samples cut parallel to the compression axis of such grains was nearly isotropic with respect to the direction of an applied magnetic field, and it was a factor of 6 smaller than that for the samples cut perpendicular to this axis (Glowa).

G. REACTIVITY

The oxide superconductors are not inert materials, but rather they are sensitive to exposure to certain gases and to surface contact with particular materials. Great care must be exercised to avoid contamination from water vapor and carbon dioxide in the atmosphere. In addition these materials are catalytic to oxygenation reactions, and these factors result in the occurrence of various chemical and other interactions, especially at elevated temperatures. The granular and porous nature of the materials has an accelerating effect on such reactions.

Samples of YBaCuO may degrade in a matter of days when exposed to an ordinary ambient atmosphere; they react readily with liquid water, acids, and electrolytes, and moderately with basic solutions. The reaction with water (Barns, Kishi, Yanzz) produces nonsuperconducting cuprates. The effects of acetone and other organics (McAnd) have been determined, and stable carboxyl groups have been found in the YBaCuO lattice (Parmi).

Hydrogen enters the YBaCuO lattice at elevated temperatures and forms a solid solution. Low concentrations have very little effect and high concentrations degrade the superconducting properties (Berni, Reill, Yang3). The effects of exposure to oxygen at elevated temperature and oxidation have been discussed several places in this review (e.g., Blend, Engle, Tara3).

The foregoing evidence for the reactivity of the oxide superconductors makes it necessary to consider methods of passivation or protecting them from long-term degradation. An epoxy coating was found to provide some protection (Barns). Coating the surface with metals can be deleterious since metals such as Fe (Gaoz1, Hillz, Weave) and Ti (Meyel) react with the surface of LaSrCuO or YBaCuO . There is evidence for the passivation of the surface of LaSr_x with gold (Meyer).

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H. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) consists of monitoring the weight of a sample during a heating or cooling cycle. For example, one might determine the oxygen content of a superconducting material by measuring its weight change in an oxidizing (O_2 or air) or reducing (e.g., 4% H_2 in Ar) atmosphere. Typical procedures consist of heating or cooling at $20^\circ C/min$. The relative accuracy of the method is about 0.005 (Ongz1). Many workers (e.g., Beye3, Hauck, Huan1, John4, Leez7, Maruc, Ohish, Ongz1, Tara7, Zhuzz) are now using TGA or differential thermal analysis (DTA) routinely during their sample preparation procedures.

I. CHECKS ON QUALITY

After a sample has been prepared it is necessary to check its quality as a superconductor. Most investigators employ the four-probe resistivity check to determine whether it superconducts, and at what temperature it transforms to the superconducting state. A sharp, high T_c transition is an indicator of a high-quality sample. Another widely used quality control method is the determination of the magnetic susceptibility of the specimen. Good quality is indicated by a sharp, high T_c transition with both the flux exclusion and flux expulsion close to $-1/4\pi$. This is, in a sense, a more fundamental check on quality since the value of the susceptibility far below the transition temperature is a good indicator of the fraction of the sample that is superconducting (see Section III-D).

In addition to its superconducting properties, it is also of interest to know the chemical composition and the structure of the specimen. The nominal composition is deduced from the relative proportions of the various cations in the starting material. Chemical analysis and some more sophisticated techniques such as XPS, electrospectroscopic chemical analysis (ESCA), and an electron microprobe that is favorable for low-atomic-weight elements are applicable here. Most investigators only report the cation concentrations in the specimen. Oxygen content is much more difficult to determine, but is important to know. Rutherford back-scattering experiments (John1, Wuzz1, Wuzz4) can provide oxygen contents, and metallography characterizes grain sizes.

The structures of the oxide superconductors described in Chapter VI are easily checked by the X-ray powder pattern method. Many articles list the lattice constants a , b , c of samples and mention whether they are tetragonal ($a = b \neq c$) or orthorhombic ($a \approx b \neq c$). Narrow lines and the absence of spurious signals indicate a good, single-phase sample. Typical X-ray diffraction powder patterns for $LaSr^*$ (Skelt) and YBa^* presented in Figs. V-3 and V-4, respectively, may be used to compare with patterns obtained from freshly prepared samples.

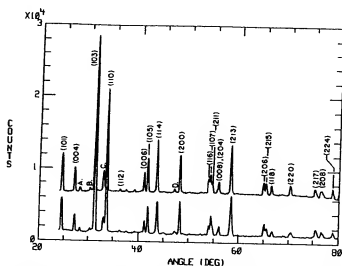


Fig. V-3. Room-temperature (upper curve) and 24-K (lower curve) X-ray diffraction powder patterns of $(\text{La}_{0.925}\text{Ba}_{0.075})_2\text{CuO}_4$ (Skell).

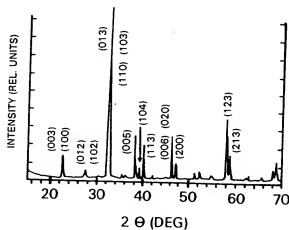


Fig. V-4. Room-temperature X-ray diffraction powder pattern of $\text{YBa}_2\text{Cu}_3\text{O}_7$. (Provided by C. Almasan, J. Estrada, and W. E. Sharp.)

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J. RESISTIVITY MEASUREMENT

A measurement of the resistance $R(T)$ or resistivity $\rho(T)$ of a material versus the temperature is the principal technique employed to determine when a material becomes superconducting. The transition temperature manifests itself by a sharp drop in resistivity to zero. The simplest way to make this measurement is to apply a voltage across the sample and measure the current flow through it, but such a two-probe method (Baszy) is not very satisfactory, and is seldom used. Most resistivity determinations are made with the four-probe technique to be described below, although more sophisticated arrangements such as a six-probe method (Kirsch) can also be used. The fabrication of low-resistance contacts by silver glazing has been reported (Vand2). These researchers pointed out the importance of a low-contact resistance ($\rho < 10 \mu\Omega/\text{mm}^2$ at 77 K) for making transport J_c measurements.

The specimen resistance as a function of temperature is generally determined in a suitable cryostat by attaching leads or electrodes to it in the standard four-probe configuration. Two leads or probes carry a known constant current I into and out of the specimen, and the other two leads measure the potential drop between two equipotential surfaces resulting from the current flow. For superconducting specimens the leads are often arranged in a linear configuration, with the contacts for the input current on the ends, and those for the measurement voltage near the center.

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BRIEF ATTACHMENT AG

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: March 14, 2005

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

THIRD SUPPLEMENTAL AMENDMENT

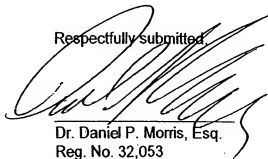
Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

The attachments referred to herein A to Z and AA are in the FIRST
SUPPLEMENTAL AMENDMENT. The Attachments AB to AG are attached herein.

Please charge any fee necessary to enter this paper and any previous paper to
deposit account 09-0468.

Respectfully submitted,



Dr. Daniel P. Morris, Esq.
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Intellectual Property Law Dept.
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ATTACHMENT AG

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The New Superconductors

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Table 8.1. Progress in Raising the Superconducting Transition Temperature T_c Since the Discovery of Cuprates in 1986

Material	T_c (K)	Year
$\text{Ba}_x\text{La}_{1-x}\text{Cu}_2\text{O}_y$	30–35	1986
$(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{Cu}_3\text{O}_{4-x}$ (at 1-GPa pressure) ^a	52	1986
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	95	1987
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	110	1988
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	125	1988
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (at 7-GPa pressure)	131	1993
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$	133	1993
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (at 30-GPa pressure)	147	1994

^aA pressure of 1 GPa is about 10,000 atm.

While this increase in T_c itself is an amazing result, a high-transition temperature is not the only property required to make new compounds useful for applications. For example if materials are to be used as wires in magnets, they must be malleable and ductile rather than brittle; in addition they must have high critical currents in large magnetic fields. Critical currents as high as those in niobium-tin have not yet been achieved in forms of the new materials that can easily be made into wires, although there are reports of comparable values in thin films on various substrates.

The Holy Grail that is being sought is a transition temperature much above room temperature. We say much above because devices must operate significantly below the transition T_c so that the critical current J_c and critical magnetic field B_c are sufficiently high. Very close to the transition temperature, the critical magnetic field is usually quite small, but we see from Figs. 3.4 and 3.5 that B_c and J_c continuously increase as the temperature is lowered below T_c . We need an operating temperature far below the critical surface in Fig. 3.15 so that both B_c and J_c are sufficiently large for the desired application.

8.3. LAYERED STRUCTURE OF THE CUPRATES

All cuprate superconductors have the layered structure shown in Fig. 8.1: The flow of supercurrent takes place in conduction layers, and binding layers support and hold together the conduction layers. Conduction layers contain copper-oxide (CuO_2) planes of the type shown in Fig. 8.2; each copper ion (Cu^{2+}) is surrounded by four oxygen ions (O^{2-}). These planes are held together in the structure by calcium (Ca^{2+}) ions located between them, as indicated in Fig. 8.3. An exception to this is the yttrium compound in which the intervening ions are the element yttrium (Y^{3+}) instead of calcium. These CuO_2 planes are very close to being flat. In the normal state above T_c , conduction electrons released by copper atoms move about on these

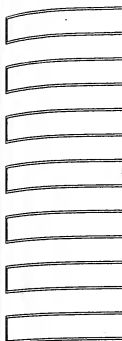


Figure 8.1. Layering scheme for different sequences for several cuprates.

Figure 8.2. Arrangement in a CuO_2 plane of the con

Transition Temperature T_c
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Year	
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t, a high-transition temperature compounds useful for applications in magnets, they must be they must have high critical igh as those in niobium-tin als that can easily be made ues in thin films on various

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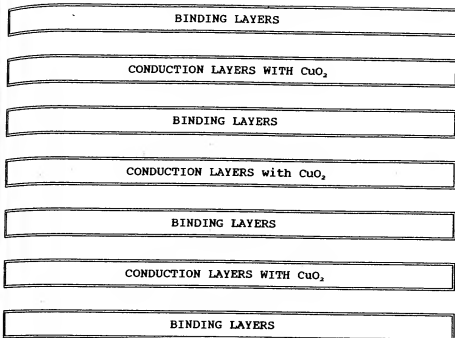


Figure 8.1. Layering scheme of the cuprate superconductors. Figure 8.3 shows details of the conduction layers for different sequences of copper oxide planes, and Fig. 8.4 presents details of the binding layers for several cuprates.

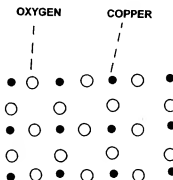
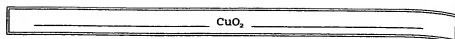
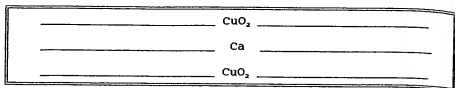


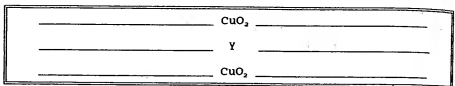
Figure 8.2. Arrangement of copper and oxygen atoms in a CuO_2 plane of the conduction layer.



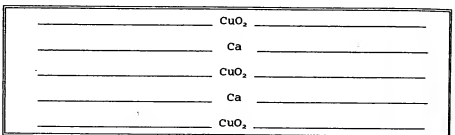
Conduction layer with one copper oxide plane



Conduction layer with two copper oxide planes



Conduction layer of yttrium compound with two copper oxide planes



Conduction layer with three copper oxide planes

Figure 8.3. Conduction layers of the various cuprate superconductors showing sequences of CuO_2 and Ca (or Y) planes in the conduction layers of Fig. 8.1.

CuO_2 planes carrying electric current. In the superconducting state below T_c , these same electrons form the Cooper pairs that carry the supercurrent in the planes.

Each particular cuprate compound has its own specific binding layer consisting mainly of sublayers of metal oxides MO , where M is a metal atom; Fig. 8.4 gives the sequences of these sublayers for the principal cuprate compounds. These binding layers are sometimes called *charge reservoir layers* because they contain



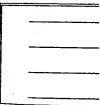
Neodym



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Bismu



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Figure 8.4. Sequence of metal ions. The parent

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two copper oxide planes

oxide planes

showing sequences of CuO_2 and

conducting state below T_c , these supercurrent in the planes. specific binding layer consisting is a metal atom; Fig. 8.4 gives 1 cuprate compounds. These *ir* layers because they contain

LaO

LaO

Lanthanum Superconductor La_2CuO_7

NdO

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Neodymium (electron) Superconductor Nd_2CuO_7

BaO

CuO

BaO

Yttrium Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$

SrO

BiO

BiO

SrO

Bismuth Superconductor $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$

BaO

TlO

TlO

BaO

Thallium Superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$

BaO

Hg(O)

BaO

Mercury Superconductor $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$

Figure 8.4. Sequences of MO sublayers in the binding layers of Fig. 8.1, where M stands for various metal ions. The parentheses around the oxygen atom O in the lowest panel indicates partial occupancy.

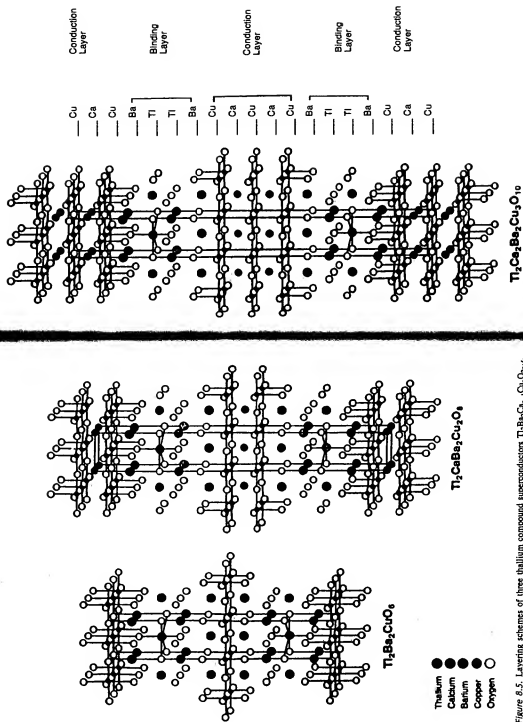


Figure 6.5. Layering schemes of three thallium compound superconductors $Tl_2Ba_2Cu_nO_{2n+2}$ where $n = 1, 2$. (O) denotes the oxygen atoms in the conduction layers. From left to right. [Adapted from Tondoli et al., Science 240, 631 (1988).]

of randomly oriented grains. In the current flow capability of

$\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$ are hole-type perovskite-copper oxide, $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{CuO}_4$ are hole-type rather than holes. The have trivalent positive ions;

(8.6)

(8.7)

tium (Sr^{2+}) and cerium (Ce^{4+}),

CuO_4 (8.8)

CuO_4 (8.9)

one extra electron to form an antiferromagnetic state. In a superconductor is hole-like. Any amount both of these examples of perovskite, but not identical structures; because most experiments are not

STRUCTURES

referred to as ceramics, they are perovskite refers to the particular perovskite, calcium titanate (Fig. 8.9) parts of the lanthanum perovskite, with Cu present in the perovskite (Fig. 8.9) positions. Similarities between these two perovskite-type

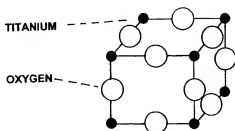


Figure 8.9. Sketch of the cubic unit cell of the mineral Perovskite, CaTiO_3 , showing titanium at the vertices and oxygen in the middle of the edges. Calcium, not shown, is in the center of the cube.

In contrast the ceramic designation is not based on structural grounds but on the similarity of the cuprate-superconducting compound and ceramic manufacturing process. For example La-Sr-Cu-O is made by heating mixtures of lanthanum oxide, strontium carbonate, and copper oxide in air at $900-1000^\circ\text{C}$ for 20 hours. Proportions of atoms in the initial mixture should be the same as in the end product, and for the compound $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$ the ratio $\text{La}:\text{Sr}:\text{Cu}$ is 1.8:0.2:1. Materials are usually ground to a fine mixture before heating; after heating in air, they are cooled, pressed into pellets, and reheated from $900-1000^\circ\text{C}$ for several more hours.

We see in Fig. 8.10 that the superconductor $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ has only one copper oxide plane in its conduction layer and each copper ion is surrounded by

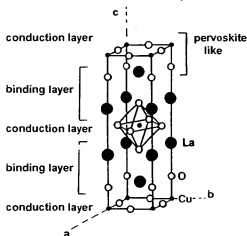


Figure 8.10. Atom positions in the tetragonal unit cell of the La_2CuO_4 compound. When strontium is substituted for lanthanum in the superconducting compound $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ it replaces lanthanum in some of the La sites.

six neighboring oxygen ions; these form an 8-sided figure called an octahedron, as shown. The CuO_6 complex of one copper and six oxygens is present in all cuprate superconductors that have a single CuO_2 plane in their conduction layer. Figure 8.11 shows atom arrangements in the mercury compound $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, which has three such planes in its conduction layer. In the upper and lower planes, copper ions have five neighboring oxygens forming a CuO_5 group with the shape of a pyramid, as shown. The middle copper ions have only four nearby oxygens, forming what is called a *square planar group* CuO_4 . If we consider removing the central copper oxide plane and one calcium layer from Fig. 8.11, we generate the two-plane structure in which all copper ions form CuO_5 pyramids. These structural details may somehow constitute important factors in determining why cuprates are such good superconductors.

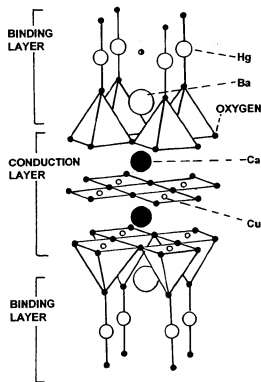


Figure 8.11. Atom positions in four unit cells of the superconducting compound $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ which has $T_c = 133$ K. The copper ions of the upper CuO_2 plane are hidden by the pyramids, and some partially occupied oxygen sites in the mercury Hg plane are not shown.

8.8. YTTRIL

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0.C
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0.C
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0.C
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Figure 8.12. First Bednorz and K. A

BRIEF ATTACHMENT AH

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIFTH SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated February 4, 2000:

ATTACHMENT 16

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of
J. Bednorz et al.

: Date: December 15, 1998

Serial No. 08/303,561

: Group Art Unit: 1105

Filed: September 9, 1994

: Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks
Washington, D. C. 20231

Sir:

I, David B. Mitzi, being duly sworn, do hereby depose and state:

That I received a B. S. E. degree in Electrical Engineering/Engineering Physics (1985) from Princeton University and a PhD. degree, in Applied Physics (1990) from Stanford University, California.

That I have worked as a research staff member in Solid State Chemistry at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1990 to the present.

That I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1990 to the present.

That I have reviewed the above-identified patent application and that I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and

YO987-074BY

Muller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
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- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect K_2NiF_4 - Type Oxides: The Compounds $La_{2-x}Sr_xCuO_{4-x/2+2\delta}$, Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite $BaLa_4Cu_5O_{13.4}$, A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.
- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$, V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: 

David B. Mitzi

Sworn to before me this 15th day of December, 1998


Notary Public

DANIEL P. MORRIS
NOTARY PUBLIC, State of New York
No. 4886876
Qualified in Westchester County
Commission Expires March 16, 1999

YO987-074BY

BRIEF ATTACHMENT AI

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIFTH SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated February 4, 2000:

ATTACHMENT 17

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of
J. Bednorz et al. : Date: December 15, 1998
Serial No. 08/303,561 : Group Art Unit: 1105
Filed: September 9, 1994 : Examiner: M. Kopec
For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks
Washington, D. C. 20231

Sir:

I, Timothy Dinger, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Ceramic Engineering (1981) from New York State College of Ceramics, Alfred University, an M. S. degree (1983) and a PhD. degree (1986), both in Material Science from the University of California at Berkley.

That I have worked as a research staff member in Material Science at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1986 to the present.

That I have worked in the fabrication of and characterization of high temperature superconductor materials from 1987 to 1991.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of

YO987-074BY

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

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That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998
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- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

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- 2) The Oxygen Defect Perovskite $BaLa_4Cu_5O_{13.4}$, A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.
- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$, V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Timothy A. Dinger
Timothy Dinger

Sworn to before me this 16th day of December, 1998

Sandra M. Emma

Notary Public

SANDRA M. EMMA
Notary Public, State of New York
No. 01PO4935290
Qualified in Westchester County
Commission Expires July 5, 2000

BRIEF ATTACHMENT AK

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIFTH SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated February 4, 2000:

ATTACHMENT 19

AK

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH
TRANSITION TEMPERATURE, AND METHODS FOR THEIR
USE AND PREPARATION

The Commissioner of Patents and Trademarks
Washington, D.C. 20231

AFFIDAVIT UNDER 37 CFR 1.132

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

I received a B.S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M.S. and PhD. degree in Materials Science (1981) from the University of California, Berkeley.

I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research

Center of the International Business Machines Corporation in Yorktown Heights, N.Y.
from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications. I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

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- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.
- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasso, Pergamon Press, 1969, in particular pages 159-186, a copy of which is attached herewith.

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- 2) The Oxygen Defect Perovskite $BaLa_4Cu_{5-0.13x}$, A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$, V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Thomas M. Shaw
Thomas M. Shaw

Sworn to before me this 14th day of December, 1998.

Sandra M. Emma

Notary Public

SANDRA M. EMMA
Notary Public, State of New York
No. 01PO4935290
Qualified in Westchester County
Commission Expires July 5, 2002

BRIEF ATTACHMENT AJ

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: March 1, 2004

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIFTH SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated February 4, 2000:

ATTACHMENT 18

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of
J. Bednorz et al. : Date: December 15, 1998

Serial No. 08/303,561 : Group Art Unit: 1105

Filed: September 9, 1994 : Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks
Washington, D. C. 20231

Sir:

I, Chang C. Tsuei, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Mechanical Engineering from National Taiwan University (1960) and M. S. and PhD. degrees, in Material Science (1963, 1966) respectively from California Institute of Technology.

That I have worked as a research staff member and manager in the physics of superconducting, amorphous and structured materials at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1973 to the present. (See attached Exhibit A for other professional employment history.)

That I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1973 to the present.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of YO987-074BY

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An

exemplary list of books describing the general principles of ceramic fabrication are:

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- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

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- 2) The Oxygen Defect Perovskite $BaLa_4Cu_{5-0.134}$, A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.
- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
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 $O_{3/2}$, V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Chang C. Tsuei

Chang C. Tsuei

Sworn to before me this 16th day of December, 1998

Sandra M. Emma

Notary Public

SANDRA M. EMMA
Notary Public, State of New York
No. 01PO4935290
Qualified in Westchester County
Commission Expires July 5, 2000

YO987-074BY

CHANG C. TSUEI

Education

California Institute of Technology, M.S. (1963), Ph.D. (1966)

National Taiwan University, B.S. (1960)

Professional Employment

1993 - present - Research Staff Member

1983 - 1993 - Manager, Physics of Structured Materials

1979 - 1983 - Manager, Physics of Amorphous Materials

1974 - 1975 - Acting Manager, Superconductivity

1973 - 1979 - Research Staff Member

Harvard University: 1980 (Summer)

Visiting Scholar in Applied Physics

Stanford University: 1982 (Sept.) - 1983 (April)

Visiting Scholar in Applied Physics

California Institute of Technology

1972 - 1973 - Senior Research Associate in Applied Physics

1969 - 1972 - Senior Research Fellow in Materials Science

1966 - 1969 - Research Fellow in Materials Science

Exhibit A

YO987-074BY

BRIEF ATTACHMENT AK

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: **NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION**

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIFTH SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated February 4, 2000:

ATTACHMENT 19

AK

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH
TRANSITION TEMPERATURE, AND METHODS FOR THEIR
USE AND PREPARATION

The Commissioner of Patents and Trademarks
Washington, D.C. 20231

AFFIDAVIT UNDER 37 CFR 1.132

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

I received a B.S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M.S. and PhD. degree in Materials Science (1981) from the University of California, Berkeley.

I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research

Center of the International Business Machines Corporation in Yorktown Heights, N.Y.
from 1984 to the present.

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- 2) The Oxygen Defect Perovskite $BaLa_4Cu_{5-0.134}$, A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

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By: Thomas M. Shaw
Thomas M. Shaw

Sworn to before me this 14th day of December, 1998.

Sandra M. Emma
Notary Public

SANDRA M. EMMA
Notary Public, State of New York
No. 01PO4935290
Qualified in Westchester County
Commission Expires July 5, 2002

BRIEF ATTACHMENT AL

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIFTH SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated February 4, 2000:

ATTACHMENT 20

AL

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J. Bednorz et al.

Date: December 18, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH
TRANSITION TEMPERATURE, AND METHODS FOR THEIR
USE AND PREPARATION

The Commissioner of Patents and Trademarks
Washington, D.C. 20231

AFFIDAVIT UNDER 37 CFR 1.132

Sir:

I, Peter R. Duncombe, being duly sworn, do hereby depose and state:

I received a B.A. degree in Chemistry from the State University of New York at New Paltz, New Paltz, N.Y. and a M.S. degree in Chemical Engineering (1983) from the State University of New York at Buffalo, Buffalo, N.Y.

I have worked as a graduate research assistant in the Chemical Engineering Department of SUNY at Buffalo from 1980-1983. I have worked as a chemical engineer in Ceramics Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, N.Y. from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications (Attachment A).

I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is attached herewith.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.
- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-181, a copy of which is attached herewith.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect K_2NiF_4 - Type Oxides: The Compounds $La_{2-x}Sr_xCuO_{4-x/2+5}$, Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite $BaLa_4Cu_5O_{13.4}$, A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., *Revue de Chemie minerale*, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$, V.S. Chincholkar et al. *Therm. Anal.* 6th, Vol. 2., p. 251-6, 1980.

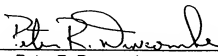
I have recorded research notes relating to superconductor oxide (perovskite) compounds in technical notebook IV with entries from November 12, 1987 to June 14, 1988 and in technical notebook V with entries continuing from June 7, 1988 to May 2, 1989. Complete copies of each of these notebooks are attached - Attachment B - Book IV and Attachment C - Book V. Below is a listing of some of the compounds I prepared and recorded in these notebooks according to the teaching as described in the Bednorz and Mueller patent application using the general principles of ceramic science as described in the books and articles listed above.

In Book IV, $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$ batch C1 pellet pressing, sintering notes and powder processing specifications start on page 2 and continue intermittently to pg. 40 (pg. 13 has superconductive susceptibility curves for pellet 9). Batch C2 $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_3$ detailed from pages 14 to 47.

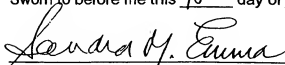
In Book V green phase (Y_2BaCuO_x) microstructural photomicrographs are logged on pages 15-17 with notes continuing to pg. 19. The perovskite superconductor BiSrCaCu oxide ($\text{Bi}_{2.15}\text{Sr}_{1.88}\text{Ca}_{1.7}\text{Cu}_2\text{O}_{8.8}$) and related perovskites $\text{Ca}_{(2-x)}\text{Sr}_x\text{CuO}_x$ and $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ synthesis notations start and continue through pg. 61 with microstructural photomicrographs.

A series of $Y_1Ba_2Cu_3O_x$ stoichiometric perturbations to study compositional effects on 2nd phase or grain boundary phases and their effect on conductivity (resistivity), sintering behavior etc., continue until the end of the book notes on the page dated May 2, 1989 (page not numbered). These are typical perovskite synthetic procedures, microstructural photomicrographs, powder processing methods, characteristic susceptibility curve(s), sintering behavior and the like. Additional notes may be available in later notebooks.

The undersigned affiant swears further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or patent issuing thereon.

By: 
Peter R. Duncombe

Sworn to before me this 18th day of December, 19 98


Notary Public

SANDRA M. EMMA
Notary Public, State of New York
No. 01PO4935290
Qualified in Westchester County
Commission Expires July 5, 2002

ATTACHMENT A

1. Compensation doping of Ba_{0.7}Sr_{0.3}TiO₃ thin films
Copel, M Baniecki, JD Duncombe, PR Kotecki, D
Laibowitz, R Neumayer, DA Shaw, TM
APPLIED PHYSICS LETTERS V73 N13 SEP 28 1998 P1832-1834
2. Method for Forming Noble Metal Oxides and Structures Formed Thereof. June 1998.
Duncombe, P. R. Hummel, J. P. Laibowitz, R. B.
Neumayer, D. A. Saenger, K. L. Schrott, A. G.
RC 98A 41575
3. Growth of Bismuth Titanate Films By Chemical Vapor Deposition and Chemical Solution
Deposition. March 1998. RC-21124
Neumayer, D. A. Duncombe, P. R. Laibowitz, R. B.
Shaw, T. Purtell, R. Grill, A.
4. Dielectric relaxation of Ba_{0.7}Sr_{0.3}TiO₃ thin films from 1 mHz to 20 GHz Baniecki, JD
Laibowitz, RB Shaw, TM Duncombe, PR
Neumayer, DA Kotecki, DE Shen, H Ma, QY
APPLIED PHYSICS LETTERS V72 N4 JAN 26 1998 P498-500
5. Contrasting magnetic and structural properties of two La manganites with the same
doping levels
McGuire, T.R. Duncombe, P.R. Gong, G.Q. Gupta, A. Li, X.W. Pickart, S.J. Crow, M.L.
J. Appl. Phys. (USA) Vol.83, No.11 1 June 1998 P7076-8
6. Effects of Annealing Conditions on Charge Loss Mechanisms in MOCVD (Ba_{0.7},Sr_{0.3})TiO₃
Thin Film Capacitors.
Baniecki, J.D., Laibowitz, RB Shaw, TM Duncombe, PR Saenger, KL Cabral C
Kotecki, DE , Shen, H , Lian, J., Ma, QY
7. Low Operating Voltage and High Mobility Field Effect Transistors Comproising Pentacene
and Relatively High Dielectric Constant Insulators RC21233(94806) 7/17/98
Dimitrakopoulos, CD Purushothaman S , Kymissis J. Callegari A. , Neumayer DA,
Duncombe PR, Laibowitz RB, Shaw JM
8. Maximum Magnetoresistance in Granular Manganite/Insulator System close to Percolation
Threshold PACS 10/06/98
DK Petrov, L Krusin-Elbaum, JZ Sun, C Feild, & PR Duncombe
9. Magnetoresistance and Hall Effect of Chromium Dioxide Epitaxial Thin Films
X.W. Li, A. Gupta, T.R. McGuire, P.R. Duncombe, Gang Xiao
10. Progress Report on High-k dielectric material: amorphous BST from solgel (09/98)
P. Andry, D. Neumayer, P. Duncombe, C. Dimitrakopoulos, F. Libsch, A. Grill, R. Wisnief

RC21352(96175)2 Dec 1998

SEND

MAIN
MENU

OTHER
OPTIONS

INCOMPLETE

Personal Inventor History

Name: Duncombe, P.R. Serial: 155139 Loc: RES YORKTOWN
Patent Pts: 36 TDB Pts: 1 Total Pts: 37 Plateau Lvl: 3
Plateau Date: 10/24/98 File Update: 11/02/98
Awards Due: None

Title: NOVEL METAL ALKOXYALKOXIDECARBOXYLATES AND USE TO FORM FILMS

06/17/98 Opened as Disc1 Y08980231 Status: Filed

06/22/98 Disc1 Review Action: File

① 09/04/98 Filed as Docket Y0998254 in US Rating: 2 Pts: 3

Co-inventors: Neumayer, D.A.

Title: SELECTIVE GROWTH OF FERROMAGNETIC FILMS FOR MAGNETIC MEMORY, STORAGE-BASED DEVICES, AND OTHER DEVICES

06/17/98 Opened as Disc1 Y08980225 Status: Filed

06/29/98 Disc1 Review Action: File

④ 10/15/98 Filed as Docket Y0998268 in US Rating: 2 Pts: 3

Co-inventors: Guha, S. Gupta, A. Bojarczuk, N.A. Karasinski, J.M.

Title: BEOL DECOUPLING CAPACITOR MATERIALS

01/28/98 Opened as Disc1 Y08980024 in US Status: Opened

06/24/98 Disc1 Review Action: File

Co-inventors: Rosenberg, R. Ning, T.H. Shaw, T.M. Edelstein, D.C. Neumayer, D.A. Laibowitz, R.B.

③ "Fabrication of Quantum Bismuth Titanate/Bismuth Titanate Multilayer Ferroelectric"
Title: FERROELECTRIC THIN FILM STRUCTURES

10/01/97 Opened as Disc1 Y08970512 in US Status: Opened

09/16/98 Disc1 Review Action: File

② 10/30/98 Sent to Counsel (L. Schuss) Co-inventors: Shaw, T.M. Neumayer, D.A. Laibowitz, R.B.

Title: CAPACITORS WITH AMORPHOUS DIELECTRICS AND IMPROVED DIELECTRIC PROPERTIES MADE USING SILICON SURFACES AS ELECTRODES

06/06/97 Opened as Disc1 Y08970261 in US Status: Opened

Co-inventors: Shaw, T.M. Neumayer, D.A. Laibowitz, R.B.

Title: FABRICATION OF THIN FILM FIELD EFFECT TRANSISTOR COMPRISING AN ORGANIC SEMICONDUCTOR AND CHEMICAL SOLUTION DEPOSITED METAL OXIDE

03/25/97 Opened as Disc1 Y08970113 Status: Filed

03/25/97 Disc1 Review Action: File

03/25/97 Filed as Docket Y0997083 in US Rating: 2 Pts: 3

03/24/98 Filed as Docket Y0997083 in JA Rating: 2

03/16/98 Filed as Docket Y0997083 in TA Rating: 2

03/12/98 Filed as Docket Y0997083 in KO Rating: 2

04/24/98 Last Office Action

Co-inventors: Parushothaman, S. Dimitrakopoulos, C.D. Furman, B.K. Neumayer, D.A. Laibowitz, R.B.

Title: NOVEL ALKOXYALKOXIDES AND USE TO FORM FILMS

10/30/96 Opened as Disc1 Y08960411 Status: Filed

03/10/97 Disc1 Review Action: File

⑤ 01/30/98 Filed as Docket Y0997069 in US Rating: 2 Pts: 3

Co-inventors: Neumayer, D.A.

Title: THIN-FILM FIELD-EFFECT TRANSISTOR WITH ORGANIC SEMICONDUCTOR REQUIRING LOW OPERATING VOLTAGES

09/11/96 Opened as Discl Y08960358

Status:Filed

03/04/97 Discl Review

Action:File

03/25/97 Filed as Docket Y0997057 in US

Rating: 2

Pts:3

03/12/98 Filed as Docket Y0997057 in KO.

Rating: 2

04/10/98 Last Office Action

Co-inventors: Purushothaman, S. Dimitrakopoulos, C.D. Furman, B.K. Neumayer, D.A. Laibowitz, R.B.

X Title: HIGH DIELECTRIC CONSTANT, BARIUM LANTHANUM TITANATE THIN FILM CAPACITORS FOR RANDOM ACCESS

06/20/96 Opened as Discl Y08960255 in US

Status:Opened

Co-inventors: Gupta, A. Shaw, T.M. Laibowitz, R.B.

Title: METHOD FOR FORMING NOBLE METAL OXIDES AND STRUCTURES FORMED THEREOF

10/30/95 Opened as Discl Y08950450

Status:Filed

11/12/96 Discl Review

Action:File

11/05/97 Filed as Docket Y0996239 in US

Rating: 2

Pts:3

10/20/98 Filed as Docket Y0996239 in JA

Rating: 2

07/30/98 Filed as Docket Y0996239 in TA

Rating: 2

Co-inventors: Schrott, A.G. Saenger, K.L. Hummel, J.P. Neumayer, D.A. Laibowitz, R.B.

Title: PEROXIDE ETCHANT PROCESS FOR PEROVSKITE-TYPE OXIDES

10/23/95 Opened as Discl Y08950434

Status:Filed

08/08/97 Discl Review

Action:File

04/08/98 Filed as Docket Y0997256 in US

Rating: 2

Pts:3

Co-inventors: Rosenberg, R. Cooper, E.I. Laibowitz, R.B.

Title: RF TRANSPONDER FOR METALLIC SURFACES

08/02/95 Opened as Discl Y08950329 in US

Status:Opened

Co-inventors: Afzali-ardakani, A. Feild, C.A. Duan, D.W. Brady, M.J. Moskowitz, P.A.

Title: METHOD FOR CLEANING THE SURFACE OF A DIELECTRIC

09/06/95 Opened as Discl FI8950292

Status:Filed

09/06/95 Sent to Evaluator

02/05/96 Evaluated

Action:Search

04/19/96 Discl Review

Action:File

12/06/96 Filed as Docket FI996047 in US

Rating: 2

Pts:3

11/29/97 Filed as Docket FI996047 in KO

Rating: 2

05/26/97 Filed as Docket FI996047 in TA

Rating: 2

06/11/98 Last Office Action

Co-inventors: Kotecki, D.E. Wildman, H.S. Yu, C. Natzle, W. Laibowitz, R.B.

Title: NANO PHASE FABRICATION OF COPPER-GLASS CERAMIC COMPOSITE VIAS IN CORDIERITE SUBSTRATES

10/05/92 Opened as Discl Y08920907 in US

Status:Published

10/08/92 Sent to Evaluator

12/17/92 Discl Review

Action:Publish

01/06/93 Mailed to Tech Discl Bulletin

09/02/93 Published

Pts:1

Co-inventors: Kang, S.K. Shaw, T.M. Brady, M.J.

Title: METHOD OF SINTERING ALUMINUM NITRODE

11/06/92 Opened as Discl FI8920668 in US

Status:Closed

11/06/92 Sent to Evaluator

12/18/92 Closed

Co-inventors: Takamori, T. Shinde, S.L.

Title: METHOD OF SINTERING ALUMINUM NITRIDE

11/06/92 Opened as Disc1 I8920667 in US Status:Closed
11/06/92 Sent to Evaluator
12/18/92 Closed
Co-inventors: Takamori, T. Shinde, S.L.

Title: ALUMINUM NITRIDE BODY AND METHOD FOR FORMING SAID BODY UTILIZING A VITREOUS
SINTERING ADDITIVE
08/13/92 Opened as Disc1 FI8920525 Status:Filed
08/17/92 Sent to Evaluator
09/29/92 Evaluated Action:Search
12/23/92 Disc1 Review Action:File
05/10/95 Filed as Docket FI992168B in US Rating: 2 Pts:3
05/28/96 Issued as Patent 5520878 in US
Co-inventors: Takamori, T. Shinde, S.L.

Title: ALUMINUM NITRIDE BODY AND METHOD FOR FORMING SAID BODY UTILIZING A VITREOUS
SINTERING ADDITIVE
08/13/92 Opened as Disc1 FI8920525 Status:Filed
08/17/92 Sent to Evaluator
09/29/92 Evaluated Action:Search
12/23/92 Disc1 Review Action:File
12/22/93 Filed as Docket FI992168A in US Rating: 2 Pts:3
01/09/96 Issued as Patent 5482903 in US
Co-inventors: Takamori, T. Shinde, S.L.

Title: GOLD DOPING OF YBA2CU3O7-8 AS A MEANS OF INCREASING TRANSPORT CRITICAL
CURRENT DENSITY
02/12/92 Opened as Disc1 YO8920161 in US Status:Closed
02/14/92 Sent to Evaluator
05/15/92 Closed
Co-inventors: Daeumling, M. Shaw, T.M.

Title: PROCESS FOR PRODUCING CERAMIC CIRCUIT STRUCTURES HAVING CONDUCTIVE VIAS
07/19/89 Opened as Disc1 YO8890552 Status:Filed
07/25/89 Sent to Evaluator
08/10/89 Evaluated Action:Search
07/30/90 Disc1 Review Action:File
12/17/92 Filed as Docket YO990091B in US Rating: 2 Pts:3
08/16/94 Issued as Patent 5337475 in US
Co-inventors: Vallabhaneni, R.V. Giess, E.A. Farooq, S. Cooper, E.I. Kim, Y.H.
Vanhise, J.A. Aoude, F.Y. Muller-landau, F. Shaw, R.R. Walker, G.F. Rita, R.A.
Neisser, M.O. Park, J.M. Shaw, T.M. Brownlow, J.M. Kim, J. Knickerbocker, S.H.

Title: VIA PASTE COMPOSITIONS AND USE THEREOF TO FORM CONDUCTIVE VIAS IN CIRCUITIZED
CERAMIC SUBSTRATES
07/19/89 Opened as Disc1 YO8890552 Status:Filed
07/25/89 Sent to Evaluator
08/10/89 Evaluated Action:Search
07/30/90 Disc1 Review Action:File
03/20/91 Filed as Docket YO990091A in US Rating: 2 Pts:3
02/01/94 Issued as Patent 5283104 in US
Co-inventors: Vallabhaneni, R.V. Giess, E.A. Farooq, S. Cooper, E.I. Kim, Y.H.
Vanhise, J.A. Aoude, F.Y. Muller-landau, F. Shaw, R.R. Walker, G.F. Rita, R.A.
Neisser, M.O. Park, J.M. Shaw, T.M. Brownlow, J.M. Kim, J. Knickerbocker, S.H.

Call your award coordinator, IPL department, or T/L 826-2680 for help.

SEND

MAIN
MENU

OTHER
OPTIONS

- T.R. McGuire, A. Gupta, P.R. Duncombe, M. Rupp, J.Z. Sun, R.B. Laibowitz, W.J. Gallagher & G. Xiao "Magnetoresistance and Magnetic Properties of $(La_{1-x})MnO_3$ Thin Films" 3M Conf. Proc: 4/96
- T.R. McGuire, P.R. Duncombe, G.Q. Gong, A. Gupta, X.W. Li & G. Xiao "Magnetoresistance & Magnetic Properties of $(La_{1-x})MnO_3$ (Vacancy) Bulk Materials" 11/96 3M conf CMR Open Forum entry
- J.Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, P.R. Duncombe, W.J. Gallagher & S. P. Parkin "Magnetotransport in Doped Manganate Perovskites" 3M conference 11/12-15/96 Atlanta, Georgia
- P. Lecoeur, A. Gupta, P.R. Duncombe, G. Gong & G. Xiao "Emission Studies of the Gas-Phase Oxidation of Mn during Pulsed Laser Deposition Manganates in O_2 & N_2O Atmospheres" JAP 80(1), 7/1/96
- J.Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, P.R. Duncombe, W.J. Gallagher & S.S.P. Parkin "Colossal Magnetoresistance in Doped Manganate Perovskites" IBM J&D to appear 1996/97
- A. Gupta, G.Q. Gong, G. Xiao, P.R. Duncombe, P. Trouilloud, Y.Y. Wang, V.P. Dravid, & J.Z. Sun "Grain Boundary Effects on the Magnetoresistance Properties of Perovskite Manganite Films"
- J.Z. Sun, W.J. Gallagher, P.R. Duncombe, L. Krusin-Elbaum, R.A. Altman, A. Gupta, Y. Lu, G.Q. Gong & G. Xiao "Observation of Large Low-field Magnetoresistance in Tri-layer Perpendicular Transport Devices Made Using Doped Manganate Perovskites" to appear Appl. Phys. Lett.
- J.Z. Sun, L. Krusin-Elbaum, P.R. Duncombe, A. Gupta & R. B. Laibowitz "Spin-Polarized Tunneling in Doped Perovskite Manganate Trilayer Junctions" APL submission 11/96
- T.R. McGuire, P.R. Duncombe, C.Q. Gong, A. Gupta, X.W. Li & G. Xiao "Interlayer Exchange Coupling & Magnetoresistance Of LCMO/LSMO 67/33 Multilayers" APL submission
- R.B. Laibowitz, T.M. Shaw, D.E. Kotecki, S. Tiwari, A. Gupta, A. Grill, & P.R. Duncombe "Properties and Applications of Thin Films of Lead Lanthanum Titanate (PLT) and Barium Strontium Titanate (BST) APS mtg 3/18-22/96
- P.R. Duncombe, S.L. Shinde, & T. Takamori "Aluminum Nitride Body Utilizing A Vitreous Sintering Additive" US05482903 1/9/96 (EF Plaque)
- P.R. Duncombe, S.L. Shinde, & T. Takamori "Aluminum Nitride Body & Method for Forming Said Body Utilizing a Vitreous Sintering Additive" US05520878 issued 5/28/96; I.A. Patent issue Award: 8/96
- Ali Afzali-Ardakani, Mike Brady, Dah-Wei Duan, Peter Duncombe, Chris Feild, and Paul Moskowitz "RF Transponder for Metallic Surfaces" Docket#: Y0895-0329 submitted: 8/2/95
- D.E. Kotecki, R.B. Laibowitz, W. Natzle, C. Yu, H. Wildman, P.R. Duncombe "Method for Cleaning the Surface of BST Prior to Electrode Deposition" Application #: F1996047 draft #1 under review
- E.I. Cooper, P.R. Duncombe, R.B. Laibowitz, "Peroxide Etchant Process for Titanate Dielectrics" Docket: Y0895-0434 rated file; in prep.
- D.A. Neumayer, P.R. Duncombe, R.B. Laibowitz, & A. Grill "Sol-Gel Processing of $BaSrTiO_3$ Films" submitted to International Symposium on Integrated Ferroelectrics (ISIF: 3/2-5/97) Santa Fe, N.M.
- A. Grill, R. Laibowitz, D. Beach, D. Neumayer & P.R. Duncombe "Effect of Base Electrode on the Crystallization & Electrical Properties of PLT" IBM RC 20402 (90185) 3/5/96
- D.A. Neumayer, P.R. Duncombe, R.B. Laibowitz & A. Grill "Effect of TiO_x Nucleation Layer on Crystallization of Sol-Gel Derived $Bi_4Ti_3O_{12}$ Films" ISIF submission 3/97
- C.D. Dimitrakopoulos, P.R. Duncombe, B.K. Furman, R.B. Laibowitz, D. Neumayer, S. Purushothaman, J. Shaw "Field Effect Transistor for Low Voltage Operation" Disclosure Y0896-0358 rated file: 9/11/96
- R.B. Laibowitz, P.R. Duncombe, D. Neumayer, K.L. Saenger, A.G. Schrott "Noble Metal Surfaces" Y0896-04xx rated "file" 10/96
- T. Shaw, R.B. Laibowitz, P.R. Duncombe & A. Gupta "High Dielectric Constant Barium Lanthanum Titanate-Based DRAM Structures" Disclosure #: Y0898-0681 rated File 5/96 in preparation
- D. Neumayer, P.R. Duncombe "Fabrication of Barium Strontium Titanate Films" Y0896-04xx rated File 10/96 in preparation

IBM Commitments:

To Win

To Execute

To Teamwork

ATTACHMENT B

IBM

T01001
Technical Notebook
Book IV

User's Initials and Last Name:

P. Duncombe

Employee Serial:

155139

Date of First Entry:

Date of Last Entry:

Security Classification:

11/12/87 6/88

MORAR

IBM Technical Notebook

11/12

70/30 - 75-25 } CLGE P2 - ~ 12:30 start

3.094¹ 0.574 0.179 4.07
1.458 0.455 0.760

"63.9" 123 basis
84.6 1?

~4 hrs

88.047
≤ ~1.5% loss

0.515 0.158
1.308 0.401 0.539

5.65

88.7 better
p1 → 83.4

11/12

ST₁O₃ - ST₃ → 32 hrs ST₂ pos. → 48

11/13 ST₁O₃ ⇒ ST₃ → coded in morning see book III, pg (A7)

4.024 0.510 ✓ 0.240 ✓ ~ 5.01 "1.04(2)% dense"
no airt loss 1.295 0.610 0.803 same Sally

~48 hrs (+ cooling 3 mornings, stepwise) sintering pellet

Cutting record

start 0.425 (0)

+ 0.060 Δ - saw (0.015) = 0.045 ~ 1.14 mm w/ flattening ~ 1 mm ✓
0.485 (Δ 0) ↳ 0.042 (1.08 mm) OK

0.060
0.545 (0.045 Δ resid; actual ⇒ 0.052 → (1.32 mm)

(55)

0.0465 (1.18 mm)

0.0523

bottom (0.6-0.69) not flat (1.52 mm)

IBM Technical Notebook

10/13
 2

PRE

STA - some security on 1 side (a slice worth)

4.178 0.584 ~0.287 3.316
 1.483 0.729 1.26

way final piece of
 STZ @ 4.55

68.9
 average

will remove Monday morning ~ 6:6 AM, 6:54 AM - 6:54 AM, ~ 63+ hours projected

10/16

4.169 0.510 ~0.250 4.98
 (0.2%) 1.295 0.635 0.837

1.035 <CONSISTENT>

G1 150-26,000 UNL-3300

4.01 0.573 0.248 0.542 3.76
 1.468 0.630 0.446

density est. (figure 65%) => 5.785 RANGE (5.371-6.217)

C1251

10/17 3300/26,000
 3.105 0.566
 1.438

EXTREMELY SHARP, flat surface, and sharp corners/pellet
 0.193(4) 3.90 61.2%
 0.490 0.796

G1 16 hrs

3.985 0.578 0.250 (exchange) 3.738 (last 0.5% density)

10:18

in hot furnace, packed $T_c = 520C$

20 T_c 977 T_s 745 T_{SET} 971 to 'push' STP

21 ↓ 838

22 898

23 935

24 949 956

2:23

2:54 495

23 1/2 → 951

~ SET-PT.

0.5% for slow cool (first stepped to 840)

The above understood

Date

and

Date

IBM Technical Notebook

3

10/17

C1251 \rightarrow pellet multiply checked as if organic residue vaporized, evidence
of vapor transport to spread plate, etc. ex. K12

2.925 10.18
3.5%

9.79 - 3.105 \Rightarrow 6.685

10/18

G1 - post 4.094 split in 4 pieces (seemingly on cooling)

G2 4.1 0.579 0.253 3.75 \checkmark pellet slightly
1.471 0.643 1.093 disfigured, broken.

33

4.155
0.510 0.220
1.295 0.559 0.736 5.64 about expected density

D.D.1 P.R.

3.10 0.5765" 0.91"

3.11 0.513 0.165 5.61 88.2
1.303 0.419 0.559

5.75

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4/11/24

Thermodyne Tube furnace set-up specs.

thermocouple: Dia. ~0.255 length 20" + ~~USED~~ 23"

Set-up complete w/ plug in jacks, ext. wire, 5 samples.

11/30 Analytical Submission

C1 - 0.75 g	$Y_{0.02}Ba_{0.98}Cu_{0.6}$	Y, Ba, Cu
C2 - 1.1	Y_2O_3	Y , trace 99%
C3 - 2.0	" BaO "	Ba ,
C4 - 1.0	TiO_2	Ti , trace
C5 - 2.0	$SrTiO_3$ pre	Sr, Ti , trace
C6 - 1.0	↓ post-mix	↓
C7 - 2.0	DRC 123	Y, Ba, Cu
C8	DD 123	Y, Ba, Cu
C9	off comp 7.11	

YIELD $\rightarrow 20.4 \text{ g}$ \therefore MUST be some from old batch or ZrO_2
COMBINED w/ OLD POWDER $\rightarrow 23 \text{ g}$ of milled powder

12/2
C1. batch 45.6 grams left
39.56 g (x6 g kept for files)
10.5
29.5 left for pellets
~ 10 long enough change TFE/toluene

NEW BOTTLES ORDERED, NO TEFLON AVAILABLE, - approx - 60 hrs total

SrTiO_3 pellets $\Rightarrow 10-10$ (29) ^{Tues} ^{circum} $\therefore 2-2\text{an}$ (12?) ^{circum} $\sim 12-12$ ^{Thurs} (24)

ST5, ST6 - start 10 AM, 12/9; numerous interruptions due to forensic malfunctions
ST5 edge chips 1 side OK otherwise 21⁺, at 12:00 PM, 12/10

*14.08 0.285 0.584
0.52

(\$01) 0.237 0.520 4.94 1.027
0.602 1.321 0.825

STG large chip Jimmy 150 pressing in $\frac{3}{4}$ size, must do

$$\begin{array}{r} 1.128 \\ 0.586 \\ \hline 0.542 \end{array} \quad \begin{array}{r} 0.886 \\ 0.297 \\ \hline 0.589 \end{array}$$

4.15 0.513 0.249 4.92 1.023
1.303 0.632(5) 0.843

*'boring' rock

The above understood
and witnessed by:

Date _____

and

Date _____

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6

950C Run						
PORT GREEN	C1P9					
	3.108	0.577	0.185	3.92	61.5	
		1.466	0.470	0.793		
PORT GREEN	3.1	0.514	0.161	5.66	88.9%	
	no loss	1.306	0.409	0.548		
PORT GREEN	DRC 2	0.579	0.177	4.19	65.8	
	3.204	1.471	0.450	0.765		
PORT GREEN	3.2	0.551	0.165	4.96	77.9	
	no loss	1.400	0.419	0.645		

pellets not in best shape after 26000 977C Run

	C1P10	0.574	0.185	3.99	61.9	
	3.090	1.458	0.470	0.785		
	3.056					
PORT	1% loss	0.508	0.157	5.88	92.3	PROBABLY 93
		1.288	0.399	0.519		+3.4%

	* DRC 3	0.579	0.181	4.24	66.6% ~	
	3.318	1.471	0.460	0.782		
PORT	crack still apparent, but holding					
	3.293	0.547	0.168	0.447	5.08	79.9 + 2%
	0.75% loss	1.389	0.427			

C1P10 Pyrometer 91.8 → 92 ∴ mostly closed porosity (95% of open pore density rates)

* cracked in 1/2 but holding. Will go up if see if it heats.
To Temp @ 4:05 → 2 HRS 6:05 ~~then~~ ramp down
9:00 AM 11/8 start cooling, OK NOT FIBERING WHEN ARRIVED, THOUGH COULD HAVE HAD BACK PRESSURE

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7/27 7

12-8

100% E/G mix \Rightarrow new wght calc.

(4.0 g) E basis (transferred to jar for physical mixing)

$$92.0913 \text{ g/mM section} \therefore \frac{4.0}{92.0913} = 0.0434 \text{ mM}$$

0.0434 mM is BASIS for MIX of 0.7 mM E ectetic

$$0.0434 / 0.7 = 0.0620 \text{ mM total} \therefore 0.3 \text{ mM } 211 \rightarrow$$

$$0.3 (0.0620) = 0.0186 \text{ mM } (94.6725 \text{ g/mM } 211) = 1.761 \text{ g } 211$$

$$\begin{array}{r} 1.761 \text{ g } 211 \\ 4.0 \text{ g } E \\ \hline 5.761 \text{ g mix} \end{array}$$

$$\text{tare } 0.83 \quad \begin{array}{r} 5.76 \\ 5.68 \text{ recovered} \\ \hline 0.08 \text{ loss on mixing} \end{array}$$

5.53 after gundng (slight loss)

1 pellet poured \Rightarrow EG1 \Rightarrow to temp 12/10 @ 3:40-45 NOT OUT TO BE 5:45

$$\begin{array}{cccc} 2.57 & 0.580 & 0.153 & 3.88 \\ 1.473 & 0.389 & 0.463 & \end{array} \quad \text{"60.9" } \Rightarrow 74\%$$

REL. density calc $0.3(6.00) + 0.7(4.9) \Rightarrow 5.23$ approx theoretical
 \uparrow EMPIRICAL D's

$$\begin{array}{cccc} 2.543 & \sim 0.611 & 0.161 & 2.825 \\ (1\% \text{ wght loss}) & 1.55 & 0.480 & 0.90 \end{array}$$

Restarted for overwrite RUN

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438. IDENTITY WASP PROV

SEE FOOTNOTES
SEE POWER ROSTER

100% PUNISH BENTLEY

H₂O

SAMPLE I.D. Faded ink DATE _____

SOURCE DJ-855 OPERATOR PRD

TOTAL WEIGHT 16.855 g. OUTGASING CONDITIONS _____

TAG WEIGHT 4.061 g.

SAMPLE WEIGHT 12.794 g.

ADDED VOLUME, v. _____

CELL HOLDER VOLUME, v. _____

$$\text{OPERATIONAL EQUATION } V_p = V_c + \begin{bmatrix} V_A \\ 1 - F_2/F_3 \end{bmatrix}$$

V_p = Volume of Powder (cc)
 V_c = Volume of Sample Cell Holder (cc)
 V_A = Added Volume
 F_1 = Ferrous Reading after Preacidifying Cell
 F_2 = Ferrous Reading after Adding V_A

DATE		DATE	
7-3-67	3-6-67	7-3-67	3-6-67
10.74.2	10.48.2	10.74.2	10.48.2
4.980	5.017	4.980	5.017
7.023	5.024	7.023	5.024
4.88	4.88	4.88	4.88
0.024 (6%)		0.024 (6%)	
2.65+5.13		2.65+5.13	
2.65+5.13		2.65+5.13	

LIX. DENSITY MONITORING

best guess - 5.9
STEREOTACTICITY
TRUE MONOMER SEWLT

SAMPLE T.O. 211 DATE 12-9-87 Rm2
 SOURCE PRD OPERATOR PRD
 DRY WEIGHT 19.662 g. OUTGAS/AC CONDITIONS 20.471
 TARE WEIGHT 4.061 g. 4.061
 SAMPLE WEIGHT 15.601 g. 16.411

$$\text{OPERATIONAL EQUATION } v_p = v_c + \begin{bmatrix} v_A \\ t - r_A/r_c \end{bmatrix}$$

V_p = Volume of Powder (cc)
 V_s = Volume of Sample Cell Holder (cc)
 V_A = Added Volume
 F_1 = Freeform Reading after Pressurizing Cell
 F_2 = Freeform Reading after Added V_A

[illegible]

SEE: QUALITY WORKSHEET

HEAT-SENSITIVE
LOW TEMPERATURE

SAMPLE I.D. 110 DATE 12-9-87 K-5
 SOURCE 12.606 OPERATOR WCD
 TOTAL WEIGHT 9.06 OUTGASING CONDITIONS 13.87
 DRY WEIGHT 8.04 9.06
 SAMPLE WEIGHT 8.04 9.06
 ADDED VOLUME 1.65 9.06

OPERATIONAL EQUATION $V_p = V_c = \begin{bmatrix} V_A \end{bmatrix}$

	105.1 - Summation
V_p = Volume of Powder (cc)	18.504
V_c = Volume of Sample Cell Cavity (cc)	5.087
V_a = Added Volume	2.419
F_1 = Freevolume Banding after Freevolume Cell	2.394
F_2 = Freevolume Banding after Added V_a	

POC (A-1) D 4.05 (12.58)
 POC 4.09 (19.38)
 18.580
 5.078
 1.298
 4.15
 3.96
 3.65

STATION NUMBER
TYPE POWER POINT

SAMPLE I.D. 123 DATE 12-9-87
SOURCE DRC OPERATION PED
TOTAL WEIGHT 21.026 g. OUTCASTING CONDITIONS _____
TARE WEIGHT 4.063 g.
SAMPLE WEIGHT 16.963 g.
ADDED VOLUME 1.3485 cc
CELLS WATER VOL % 100

$$\text{OPERATIONAL EQUATION } v_p = v_c + \left[\frac{v_A}{1 - \beta_{\text{eff}}/r_p} \right]$$

V_p = Volume of Powder (cc)
 V_c = Volume of Sample Cell Holder (cc)
 V_A = Added Volume
 P_1 = Pressure Reading after Pressurizing Cell
 P_2 = Pressure Reading after Added w

	Page 1	Page 2	Page 3
R-3.6625	R-3.6625		
1. 18.598	18.596		
2. 5.077	5.077		
3. 2.93 cc			
4. 6.31 = cc			

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III. SECURITY WORKSHEET

STANDARD FORM NO. 64 THIS FORM, SECURITY

SAMPLE I.D. 193-344 DATE 12-9
SOURCE 193-344 OPERATOR CRD
TOTAL WEIGHT 19.700 g. OUTGASING CONDITIONS
TARE WEIGHT 4.641 g.
SAMPLE WEIGHT 15.059 g. ADDED VOLUME 0.857 cc
CELL HOLDER VOLUME 0.857 cc

$$\text{OPERATIONAL EQUATION } V_p = V_s \cdot \left[\frac{V_0}{1 - V_0/V_1} \right]$$

V_p = Volume of Powder (cc)
 V_s = Volume of Sample Cell Holder (cc)
 V_0 = Added Volume
 V_1 = Pressure Reading after Pressurizing Cell
 V_2 = Pressure Reading after Added V_0

R-3.646
REV. 1
DATA
R-3.646
REV. 1
REV. 1
 V_0 18.603 18.641 18.641
 V_1 5.091 5.091 5.091
 V_2 2.521 cc cc cc
SECURITY 6.493 -cc -cc -cc
in page

15

III. SECURITY WORKSHEET

STANDARD FORM NO. 64 THIS FORM, SECURITY

SAMPLE I.D. 193 DATE 12-9
SOURCE CR OPERATOR CRD
TOTAL WEIGHT 27.949 g. OUTGASING CONDITIONS
TARE WEIGHT 4.641 g.
SAMPLE WEIGHT 23.308 g. ADDED VOLUME 0.857 cc
CELL HOLDER VOLUME 0.857 cc

$$\text{OPERATIONAL EQUATION } V_p = V_s \cdot \left[\frac{V_0}{1 - V_0/V_1} \right]$$

V_p = Volume of Powder (cc)
 V_s = Volume of Sample Cell Holder (cc)
 V_0 = Added Volume
 V_1 = Pressure Reading after Pressurizing Cell
 V_2 = Pressure Reading after Added V_0

R-3.646
REV. 1
DATA
R-3.646
REV. 1
REV. 1
 V_0 18.603 18.641 18.641
 V_1 5.091 5.091 5.091
 V_2 2.521 cc cc cc
SECURITY 6.493 -cc -cc -cc

16

III. SECURITY WORKSHEET

STANDARD FORM NO. 64 THIS FORM, SECURITY

SAMPLE I.D. 193 DATE 12-9-87
SOURCE CR OPERATOR CRD
TOTAL WEIGHT 19.343 g. OUTGASING CONDITIONS
TARE WEIGHT 4.641 g.
SAMPLE WEIGHT 14.702 g. ADDED VOLUME 0.857 cc
CELL HOLDER VOLUME 0.857 cc

$$\text{OPERATIONAL EQUATION } V_p = V_s \cdot \left[\frac{V_0}{1 - V_0/V_1} \right]$$

V_p = Volume of Powder (cc)
 V_s = Volume of Sample Cell Holder (cc)
 V_0 = Added Volume
 V_1 = Pressure Reading after Pressurizing Cell
 V_2 = Pressure Reading after Added V_0

R-3.646
REV. 1
DATA
R-3.646
REV. 1
REV. 1
 V_0 18.677 18.641 18.641
 V_1 5.208 5.208 5.208
 V_2 1.703 cc cc cc
SECURITY 6.10 -cc -cc -cc

AUT. DOC. TO 1420

15

STANDARD FORM NO. 64 THIS FORM, SECURITY

SAMPLE I.D. CRD DATE 12-10-87
SOURCE CR OPERATOR CRD
TOTAL WEIGHT 6.613 g. OUTGASING CONDITIONS
TARE WEIGHT 4.641 g.
SAMPLE WEIGHT 1.972 g. ADDED VOLUME 0.857 cc
CELL HOLDER VOLUME 0.857 cc

$$\text{OPERATIONAL EQUATION } V_p = V_s \cdot \left[\frac{V_0}{1 - V_0/V_1} \right]$$

V_p = Volume of Powder (cc)
 V_s = Volume of Sample Cell Holder (cc)
 V_0 = Added Volume
 V_1 = Pressure Reading after Pressurizing Cell
 V_2 = Pressure Reading after Added V_0

R-3.646
REV. 1
DATA
R-3.646
REV. 1
REV. 1
 V_0 18.186 18.186 18.186
 V_1 5.208 5.208 5.208
 V_2 0.455 cc cc cc
SECURITY 6.099 -cc -cc -cc

CRD 956
677-51.8-42

16

7.648 - 18.75

The above understood
and witnessed by

Date

and
by

Date

IBM Technical Notebook

10/12/10

Powers for Analysis \Rightarrow Never entered @ Conf. Time
~~Specs~~ Derivation
~~Y₂O₃~~ left exposed to air 12/11, Sensitive NOT Enough
 Need to increase by 10X at least.

TiO₂

C1 $\frac{4BaCu}{1123}$

DD1

DRC

P11

EI

$\frac{1}{2} Ba_{0.23} Cu_{1.6}$

off comp

off comp

Table 1 - Precision¹ of Metals determined by ICP in La_{1-x}Sr_xCuO₄ and YBa₂Cu₃O₇ Thin Films.

Element	x ²	S.D.	R.S.D. (%)
La	1.80	0.08	4.54
Sr	0.20	0.01	5.52
Cu	1.00	0.14	3.52
Y	1.00	0.05	5.60
Ba	2.04	0.07	3.43
Cu	3.00	0.11	3.67

¹Based on 7 determinations

²Calculated atomic ratios

For 123

Y (0.33) $\Rightarrow \pm 0.019$ 0.311 - 0.352

Ba (0.66) $\Rightarrow \pm 0.023$ 0.641 - 0.677

Cu (1.00) $\Rightarrow \pm 0.056$ 0.943 - 1.056

Theoretical wgt % calcs.

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$TiO_2 \Rightarrow 47.90/79.8988 \rightarrow 59.95$

Anal

57.3

error reported.

$SrCO_3 \Rightarrow 87.62/147.62935 \rightarrow 59.35$

ACT ANALYZED

$BaCO_3 \Rightarrow 137.34/197.34435 \rightarrow 69.59(2)$

$BaO \Rightarrow$

89.566

88.9

99.26 !

$SrTiO_3 \Rightarrow Sr \Rightarrow 47.74(5)$
 $Ti \Rightarrow 26.10(1)$

M.W. 183.5182

(

C5- 22.2
49.4

Ti
 Sr

85.05% (15% poor)
"3.48% rich"

C6 24.2
50.6

Ti
 Sr

92.72 (7.3% poor)
"5.98% rich"

86.5
92.5

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12/19 both well shaped pellets

C1P11 - 15026

3.673 0.574 0.215 4.03 63.3
1.458 0.546 0.9116

92% final from T.S.HAW

C4P(#)? 15026

3.058 0.560 0.206 3.606 56.6 as usual
1.437 0.523 0.848

- final microstructure full of liquid, bimodal g.s. } cracking
- no final density recorded

12/16 pellets as Source from 12/14 in apuere.
To temp (10°C/min ramp from RT) @ 10:50 A.M.
Low (loading) side undershoot 974 high (downside) overshoot 978.
Stable variation 974-976 ✓

Start ramp down 1:00 p.m. (to 600C where soak for 48 hours)

$$\left\{ \text{Discoef: } 2 \times 10^{15} \frac{\text{m}^2}{\text{s}} \times 2 \times 10^{15} \frac{\text{m}^2}{\text{s}} \times \frac{H^2}{(0.3048 \text{ m})^2} = 2.153 \times 10^{-14} \right\}$$

H²/s²

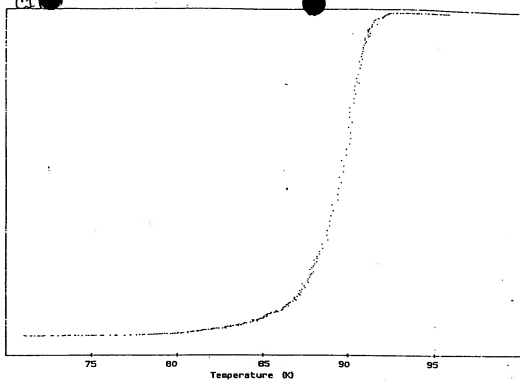
0.00

C1

13

 ΔI

0.17

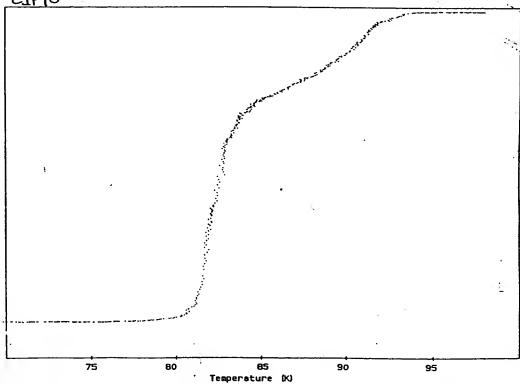


0.00

C1P10

 ΔI

-0.17



The above understood
and witnessed by

Date

and
by

Date

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14 C2 Batch \rightarrow $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{O}_7$ 200gFrom C1 batch calc, (pg. 54 Book III) \rightarrow 72 Book II $\text{Y}_2\text{O}_3 \Rightarrow$ wt. frac. \Rightarrow 17.1535 \Rightarrow 17.1707 \Rightarrow x2 \Rightarrow 34.34 $\text{BaCO}_3 \Rightarrow$ 48.5934 100 \Rightarrow x2 93.1868 BaCO_3 conversion: 93.1868 $\frac{197.35}{153.34} = 119.932(3) \div 0.99 \Rightarrow$ 121.14(4) $\text{CuO} \Rightarrow$ 36.25(31) \Rightarrow 36.2893(1) \Rightarrow x2 \Rightarrow 72.57(9)O.K. everything is Ba rich by analysis, so why not not correct \Rightarrow 119.93Apply $\frac{1}{2}$. BaCO_3 tare: $\frac{279.67}{120.59} = 2.319$
400.21 \Rightarrow 119.93 \Rightarrow 120.54reads: 120.57(4-6) was $\frac{4}{5}$ CuO tare: 0.8717
reads: 72.58 \Rightarrow 72.57(9)

transferred quant. tare to zero up paper

34.34/5 \Rightarrow $\frac{4}{5}$ transferred quant
paper weighs 0.1 what checked due to static glove charge
but after glove/charge removal 0.00. Think OK since
cal-splashed glove while (not more than 0.3% error)Expected } 227.46 g dry
tolerant } $\text{BaO} - 5.72 \text{ g/c}$ $\text{BaCO}_3 - 4.43$ $\text{Y}_2\text{O}_3 - 3.01$ $\text{CuO} - 6.3 - 6.49$ \therefore if pumping occurs w/ selective loss, BaCO_3 should preferentially be lost if not ~~well~~ uniformly suspended.

{12/21}

12/17-18 CENTUR STiO₃ RUN

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2100-1700 psi At usage 16 hr soak @ 1800 w/ $\Delta 500$ psi
w/ 56.7 up/400 down rate

Running Si-Chaisty RUN Prog. 05

So for 12/21 \Rightarrow (*) STiO₃ RUN 24 hrs \Rightarrow 1000 psi

$\frac{16}{40 \text{ hrs}} \Rightarrow 1500 \text{ psi}$ max permissible

Set for 36 \Rightarrow Ramp up started @ 4:25 p.m. 12/21

$\frac{3}{4:25}$ hrs to temp
36 hours soak
40:25

1600 psi @ 300C ramp up. $\frac{4.25}{44.5 \text{ hours total}}$ should be O.K.

(3 hrs \Rightarrow 1000) \Rightarrow 15,000 projected usage.

12/22 9:00 AM

19.3 soak hours left \therefore $\Delta t \Rightarrow 16.7 + 3 \Rightarrow 19.7 \{ (16 - 11250) \text{ psi} \Rightarrow 4750$

$\therefore 241.1 \text{ psi/hr.}$ $19.3 + 4.25 = 23.55 (241.1 \text{ psi/hr}) = 5,680$

$11250 - 5680 = \text{remainder of } 5,572 \text{ psi}$ } could run longer if rate remains constant

6:00 PM

$11,250 - 9,000 \Rightarrow 2,250 / (16.7 - 10.2) = 2250 / 6.5 = 346.2 !$

$346.2 (10.2 + 4.25) = 45,000 \text{ psi} + (9000) = 4,000 \text{ to spare} \checkmark$

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17

12-22

C2 RXN SEEMS GOOD, NO APPARENT LIQUID, LARGE SHRINKAGE
NO VISIBLE GREEN, GOOD BLACK COLOR, BEFORE UNLOADING.
~~Post weight.~~

crux #1

loss calc.

initial 166.97
time 86.21
80.76
100% expected weight 227.46 theoretical product

$$80.76 + (80.76 \times (-0.1182)) = 71.214$$

$$\frac{120.54}{227.46} = 0.52994 \text{ wt \% } \text{BaCO}_3$$

crux #2
initial

172.72
94.98
77.74

$$\frac{153.34}{197.35} (0.52994) = 0.41176$$

above

$$= 68.551$$

$$\Delta = 0.52994 - 0.41176 = 0.1182\% \text{ total loss?}$$

crux #3

173.46
105.17
68.29

above

$$= \frac{60.218}{109.983} \text{ total} / 0.997 = 200.58 \checkmark \text{ OK.}$$

Actual yields - 1A H2 RXN @ 940C

crux #2	170.45	total weight	above expected	% RXN
2.27g weight loss	94.98	initial time	weight	
	89.49	75.47	6.919	24.7
			(9.489)	

crux #1	169.92	total weight	above expected	% RXN
2.08g weight loss	86.21	initial time	weight	
	78.71	78.71	7.496	21.5
			(9.546)	

crux #3	171.91	total weight	above expected	% RXN
1.55g weight loss	105.17	initial time	weight	
	66.74	66.74	6.522	19.2
			(8.072)	

21.8% OK.

The above understood

Date

and

Date

Date

18. Recheck of wght bxs calc.

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$$\begin{array}{r}
 B_0 \quad 137.34 \\
 0 \quad 15.9994 \\
 \hline
 153.3394 \\
 \sim 153.34
 \end{array}
 \quad
 \begin{array}{r}
 B_0 \quad 137.34 \\
 30s \quad 47.9982 \\
 \hline
 12.0185 \\
 197.34935 \\
 \sim 197.35
 \end{array}$$

$$\frac{153.34}{197.35} = 0.776995 \quad (120.54) = 93.6589999 \quad 126.881 \text{ g}$$

$$26.881 \text{ g} / 3 \text{ crux} = \sim 8.96 \text{ g/cruxible} \sim \text{correct}$$

Individual wght increases during grinding

12/29

crux 3 66.72 unloaded

$$\begin{array}{r}
 105.17 \text{ tare} \\
 171.82 \text{ loaded} \\
 \hline
 171.91 \\
 + .09 \text{ g} \\
 \hline
 66.74 \text{ g}
 \end{array}
 \quad
 \begin{array}{l}
 \text{previously} \\
 \text{loss} = 0.135\%
 \end{array}$$

$$\begin{array}{r}
 169.38 \\
 171.82 \\
 \hline
 -2.44 \text{ loss} \\
 + -1.55 \\
 \hline
 3.99
 \end{array}$$

$$\begin{array}{r}
 \text{crux } 2 \\
 86.20 \text{ tare} (-0.19/20) \\
 78.75 \text{ load } (-0.02/20) \\
 78.69 \text{ gone after grinding} \\
 + .06 \text{ g} \\
 \hline
 164.85 \text{ g} \\
 78.65 \text{ loss } 0.09 \text{ g loss} = 0.08\% \text{ loss}
 \end{array}$$

$$\begin{array}{r}
 161.68 \\
 164.85 \\
 \hline
 -3.17 \text{ loss} \\
 + -2.27 \\
 \hline
 5.44 \text{ total loaded}
 \end{array}$$

$$\begin{array}{r}
 \text{crux } 1 \\
 75.49/8 \text{ unloaded} \\
 94.99/8 \text{ tare} \\
 75.46 \text{ load (precise)} \\
 \hline
 170.44 \text{ loaded} \\
 75.46 \text{ 0.03 loss}
 \end{array}$$

$$\begin{array}{r}
 167.18 \\
 170.44 \\
 \hline
 -3.26 \text{ loss} \\
 + 2.05 \\
 \hline
 5.31
 \end{array}$$

The above understood and witnessed by

Date

and

Date

IBM Technical Notebook

19

Samples were incompletely converted, as right loss indicated. Top was black but went through a transition of greens progressively lower in crucible. Ground purity was a dull forest green. Cux 1 slightly darker than 2 & 3. All had rather hard oxide particles (presumably Fe_2O_3). Tops exhibited orange flow throughout crucible. No fogs used in second run. Heat treatment.

2/29 New losses consistent w/ cux loading. Conversion now up to 70.8 ~ 71%. Still reground and reweighing loss

cux 2
unloaded 95.02
ground 72.10

cux 1 86.25 ✓
grd. 75.40

cux 3 105.19
grd pot 64.15

cux 1 } 192.24 } 188.21 -4.03 22.82 expected 26.807 (85.1%)
(3 crucibles) } 86.29/1

cux 2 } 199.53 } 195.48 -4.05
95.01

Reground, to 1 crucible

$$\% (202.47 - 199.73) = 2.74 \text{ g loss } (1.35\%)$$

286.00
86.27
199.73 of 202.47 to start
(before grd)

The above understood

Date

and by

Date

20 123 Night Loss Summary IBM Technical Notebook

Circled #	Initial	Post (1)	Post (2)	Post (3)	Circled
1	80.76	78.71	75.48	102.0	143
2	77.74	75.47	72.20	100.47	2
3	68.79	66.74	64.21	202.47	
Sheet	226.79 227.46	220.92	211.89		

Final grad into 1 canille: pre 202.47
grad post 199.73
loss 2.74g (1.35% \Rightarrow 1g spill of saved push)

Was 85% ready before this run.
Total loss so far slightly less than 2432g / 27.46 (88.5-85%)

Expect less than, but approx. 3.0 g loss for complete run.

0.52994% BeCO_3 { (0.77995% of BeCO_3 is BeO)

Look for 283g total upon cooling!

1/5 initial weight. 59.1
post 288.00
287.17
001.83g

199.93 initial
197.59 unloaded
2.14

1/4 Sr.TiO₃ synthesis IBM Technical Notebook references book III pgs. 77, A3

21

TiO₂ - 79.8988 g/m

SrCO₃ - 147.6235

SrTiO₃ - 183.5182

SrO - 103.6194

Ti - 47.90

IN SrTiO₃ 26.1009

Sr - 87.62

IN 47.4446

Take transferred AMOUNT TO SHAKER JAR (SrCO₃) as basis for TiO₂ addition

$$201.66 \text{ g base} \times \frac{48.60}{147.6235} \times 2.328 \left(\frac{6}{4} \right) \text{ moles} \times 79.8988 \frac{\text{g}}{\text{m}} \text{ TiO}_2 = 26.2499$$

$$= 26.2541$$

~~110.85~~

251.07

202.56

48.51

251.07

251.07

26.25 / 999 = 26.2763

277.32

target 277.357

46

actual 277.3576

22

IBM Technical Notebook

CONFS SCRIPT A1 dated 87/12/02 14:32:25 Page 1

Date: 2 December 1987, 13:24:31 EST
From: PLECHAT at YNYNE
To: FPD

The laboratory results on your samples are:

# C1	Y	Ba	Cu O	Cu=1	ICP
	0.93	0.68	X		
# C2	Y	...	78.1 X (V/W)		
# C3	Ba	...	88.9 X		
# C4	Ti	...	57.3 X		/ error due to static electr. during weighing of sample!
# C5	Ti	...	22.2 X		
	Sr	...	49.4 X		
# C6	Ti	...	24.2 X		
	Sr	...	59.6 X		
# C7	Y	Ba	Cu O	Cu=1	
	0.34	0.71	X		
# C8	Y	Ba	Cu O		
	0.34	0.71	X		
# C9	Y	Ba	Cu O		
	2.37	1.10	X		

IMP

Date: 21 October 1987, 10:45:18 EST
From: PLECHAT at YNYNE
To: FPD

The laboratory results on your samples are:

# C1	Y	Ba	Cu O	Cu=1	ICP
	0.35	0.72	X		
# C1f	Y	Ba	Cu O		
	0.33	0.70	X		
# C5	Y	Ba	Cu O		
	2.21	1.06	X		

Other results to follow from Olson.

IMP

Note: I have produced a light green compound from 123 with
the formula: Y Ba Cu O. If interested get in touch
with me. 12 3 X

heretical
T₁ considerably low 26.1
Sr considerably high 49.7

The above understood
and witnessed by

Date

and
by

Date

IBM Technical Notebook

2:

41
282.17
tare 86.61
196.56

written 197.59
196.36
1.03 g lost during grinding

Post
196.56
194.16
-2.40

Lost another 2.4 g. Must be totally converted @ this point.

Uniaxial - 7,000 / 0.371 = 18,870 PSI

0.126 0.161 2.53 4.19 65.8
0.320 1.55 0.604

C2P1 green
not final ans. 2d

C2P2 → Will leave notes on pusher before too busy. Still see 110. on crucible however, distorting.

↳ 1 mill 4.2 μm PSD 10-1 ~ flat dist.

gun 27150 pressed

3.59 0.580 0.194 4.274 67.1% (high vs C1)
1.473 0.493 0.84

C2P3 - mill 2 2.53 μm ave., much better behind pellet

3.55 0.576 0.210 3.96 62.2% (good decrease up C1)
1.463 0.533 0.896

C2P2 - removed @ 600°C ⇒ 20° up to 800, 10° to 975, 20° down

3.59 0.554 0.186 4.89 76.8% 1 terrible
1.407 0.472 0.734 stable under heat

1/3

C2P3 3.57 0.517 0.185 5.57
1.313 0.47 0.636

plotted attention
87.4%

~ 88

IBM Technical Notebook

24 1/13

C2P4 3,775 WML/26,000 15C

1 tens unit 996 peak
 988 2HRS/100 over

3.50/1 0.576 0.206
 1.463 0.523

3.987 62.6% consistent

1/14 3.49

0.515 0.180
 1.308 0.457

0.614 5.68 89.2

C2P5 3,775/24

3.18 0.577 0.199
 1.466 0.505

990 3.74 58.7%

3.15

0.496 0.168
 1.26 0.427

0.532 5.92 92.9

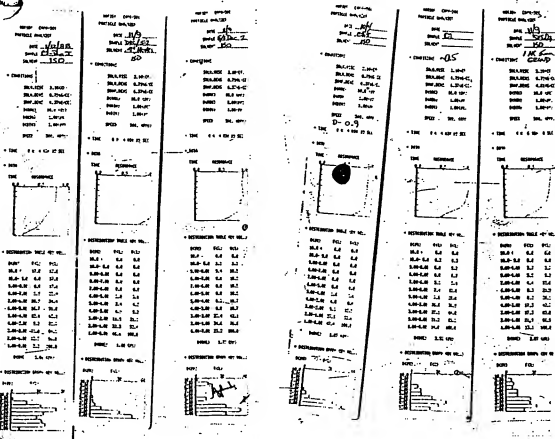
pellet has stages cracking and volume microfracturing with
 large grain interior and peripheral agglomeration of small grains.

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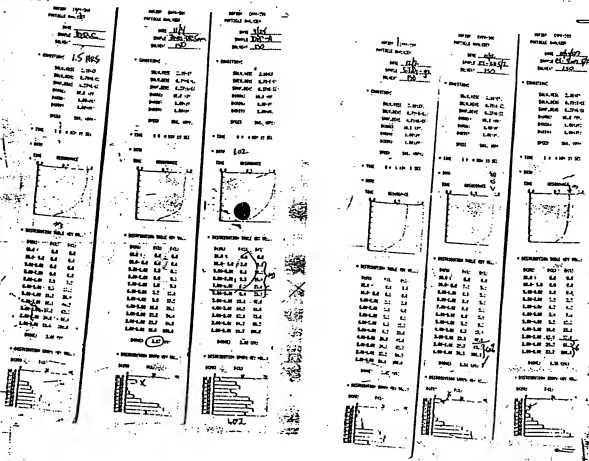
25

PSD

SHEETS



↑
see pg 217
for REST



The above understood
and witnessed by _____

Dystro

and
by

Date _____

Date and sign every entry. Have entry witnessed. Submit in anything possibly new arrive.

ssibly important
losure of

1100 Page 10
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 Register with local Recorder

IBM Technical Notebook

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Page III	Page II	Page I	Page I
<p>NAME: [Name]</p> <p>DATE: [Date]</p> <p>TIME: [Time]</p> <p>LOCATION: [Location]</p> <p>TEST: [Test]</p> <p>RESULTS: [Results]</p> <p>CONCLUSION: [Conclusion]</p>	<p>NAME: [Name]</p> <p>DATE: [Date]</p> <p>TIME: [Time]</p> <p>LOCATION: [Location]</p> <p>TEST: [Test]</p> <p>RESULTS: [Results]</p> <p>CONCLUSION: [Conclusion]</p>	<p>NAME: [Name]</p> <p>DATE: [Date]</p> <p>TIME: [Time]</p> <p>LOCATION: [Location]</p> <p>TEST: [Test]</p> <p>RESULTS: [Results]</p> <p>CONCLUSION: [Conclusion]</p>	<p>NAME: [Name]</p> <p>DATE: [Date]</p> <p>TIME: [Time]</p> <p>LOCATION: [Location]</p> <p>TEST: [Test]</p> <p>RESULTS: [Results]</p> <p>CONCLUSION: [Conclusion]</p>

The above understood

Date

and

Date

IBM Technical Notebook

28 1/A (18, 17, 14, 15 26 1/2)

NOTE: C1 powder

C1P12, 13, 14, 15 3.775/26.5

C1P12

3.04	0.574	0.178	3.92	61.5%
1.478	0.452	0.7755		
3.01	0.506	0.153	5.966	93.66%
1.285	0.387	0.509(5)		

C1P13

3.00	0.574	0.175	3.93(4)	61.8%
1.478	0.444(6)	0.7626		
2.97	0.506	0.150	6.01	94.35
1.285	0.381	0.494		

C1P14 (X)

2.89	0.574	0.169	3.92(7)	61.6%
1.478	0.429	0.736		

C1P15 (X)

3.05	0.575	0.129	4.00	62.8%
1.460(8)	0.455	0.762(8)		

(X) NO DATA ON final pellets - Tons tack

IBM Technical Notebook

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1/9 RUNS IN FURNACE at: all RAMPs 10C/min

2 HRS
SURFACE 1
(12) (13)
SURFACE 2
(14) (15)

SINTER TIME

1/9 A.M.



4:10 PM

4:25 PM

to temp (975°C)

6:18 PM

RAMP down to 600C soak

1/20

1:19 PM

RAMP down to RT

check

2:22 (270C)

Pellet thickness experiment

DT mill powder

3775/26,000

DT 2.0

2.04

0.575

0.119

4.03

63.3 %

2.01

1.460(5)

0.302

0.506

0.507

0.100

6.09

1.288

0.234

0.33

95.6

DT 1.5

1.54

0.575

0.090

4.01

62.95 %

1.51

1.460(5)

0.229

0.384

0.509

0.075

6.04

94.8

1.293

0.190(5)

0.250

DT 1.0 K

1.09

0.575

0.065

3.95

62.0 %

1.460(5)

0.165

0.276

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and witnessed by

Date

and
by

Date

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Cutting Calculations for C1P12, 13

$$\begin{array}{r} 0.308 \\ 0.06 \\ \hline 0.048/3 = 0.016 \end{array}$$

3 blade thickness + 0.05

C1P12 (0.025) 5 = 0.125
 (6 = 0.150 ← O.K. from micrometer

use 2 cuts { no 'paralleling'

$$\begin{array}{r} 0.060 \\ 0.040 \\ \hline 0.11/3 = 0.037 + 0.015 = 0.052 \end{array}$$

12. From edge

1 cut made, BUT PELLET HAS CRACK

$$\begin{array}{r} (0.025) 6 = 0.150 \\ 0.040 \\ \hline 0.11/3 = 0.037 + 0.015 = 0.052 \end{array}$$

1/21

DT 1.751 in furnace/no green data (5°C ramp to try to eliminate sinter-cracking)

DT 1.75(2)

1.88

2.575

0.111

3.92

62.5

never run

1.465

0.282

0.472

IBM Technical Notebook

31

Stereopycnometer

1/27/88 {25/26 supply, miller repair}
28
29 2/01

See sheets

Data Points (Multiples)

"83"	D _A	DEC, DDP12	D _P
82.95			95.8
"86"	86.4	JPL2, CIP3, CIP2	92.2
"89"	89.3	CIP1, CIP4, CIP7	89.56
"91"	91.3	CIP1, CIP5, CIP8	91.9

USE pad: 99.3-95.8

$\Delta 86.4 - 89.3 = \Delta 3\%$

Single Point trends

87.5	87.5	JPL	83	seems to not clear, just to closed
77		CIP2	95.4	definitely and open d
"93"	93	DDP13	86.6	indicates closure

⊗ small volumes yield low D values for closed porosity.

32

3500/26,000

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2/02 Sintering: Porosity Inquiry C1 & C2 @ 975
{ 10/min ramp from RT, 2 HOUR SOAK, 10/ → to RT NO
O₂ equilibration. In order from left to right in row,

C1P16

3.03	0.575	0.178		4.00	62.8	} polished
	1.460(5)	0.452	0.757			
3.00	0.508	0.157		5.92	92.9	
	1.293	0.386	0.507			

C1P17

3.26	0.575	0.191		4.01	62.9(5)	} polished
	1.460(5)	0.485	0.812(5)			
3.22	0.508	0.164		5.94	92.8	
	1.290	0.4166	0.544(5)			

C2P6

3.16	0.575	0.191		3.82(6)	60.0	} polished
	1.460(5)	0.493	0.826			
3.11	0.497	0.160		6.42	96.1	
	1.262	0.406	0.507(8)			

C2P7 ^{chip}

3.21	0.575	0.199		3.79	59.5	} polished
	1.460(5)	0.505(5)	0.847			
3.16	0.497	0.164		6.065	95.2	
	1.262	0.4166	0.521			

C2P7 good & dense, but exterior cracking due to oxygen penetration.
Will guide cool by opening furnace. Quench.

The above understood
and witnessed by _____

Date _____

and
by _____

Date _____

IBM Technical Notebook

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ITM

C2-8	3.08	0.573	0.191	3.82
		1.455	0.48	0.2010
3.065	0.529	0.158	5.53	
		1.328	0.399	0.553

59.97 \rightarrow ~60%
comparable to previous
86.8

C1-18	3.07	0.578	0.178	4.01
		1.468	0.52	0.765
3.03	0.497	0.158	6.04	
		1.267	0.401	0.5016

62.95 ~63%
comparable to previous
94.8

2/12

HP-4 green 5,000/27,000

13.98	0.947	0.301	4.025
2.105	0.764(5)	3.473	63.2

Wing C2-8 dry
st 0.50

Boat Spots \rightarrow positioning I.D.

2/15

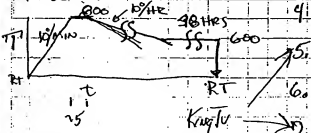
1-2-3-4-5-6-7

1. large grain material

C2 3/4

Heat Treatment

3. C2 add w/ surface cracking (outer)
4. inner surfaces should be dark



Good C2 top slice - no surface cracking
middle slice of 3/4 (w/ chip)
bottom slice of C2-5 above

START: 4:50 PM 2/12 \rightarrow 5:15 start ramp down 20HRS to soak posm
2/15 3:00 ~30HRS
QUENCH 2:50 2/15

The above understood and witnessed by

Date

and by

Date

IBM Technical Notebook

34 2/17 3500/26750

C2-9	3.09	0.575	0.193		3.76	59.0%
		1.460(5)	0.190	0.821		
	3.06	0.510	0.168			85.5
		1.295	0.127	0.562		!

C2-10	3.06	0.575	0.191		3.77	59.2%
		1.460(5)	0.185	0.812(5)		
	3.06	0.501	0.164		5.77	90.6
	3	1.272(5)	0.117	0.530		89.6

Furnace Dr purge > 1 HR @ 29⁽³²⁾ 12:10 P.M. ∴ 945/10 =
 $94.5 \text{ mins} / 60 \text{ min} / \text{HR} = 1.575 \text{ Hrs}$ OR 1 hr 34.5 mins (1:45 START
 1:45 - 2:15 (1/2 hr SINTER) w/ guard. SINTER)

C2-11	3.02	0.575	0.188		3.75	59.3% OK
		1.460(5)	0.177(5)	0.80		
	2.98	0.505	0.159		5.71	89.64 ~90
		1.283	0.109	0.522		

D3 4 μ m D3 6 μ m
IBM Technical Notebook

D3 6-7 D3 9

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NOTE: CPM-540
PARTICLE ANALYZER

FILE 2.18
SAMPLE C2-III CT
SOLVENT 150
D = 0.85

* COUNTING

SOLV. FISC 2.16 CP+
SOLV. FISC 0.7516-0.2
SAMP. FISC 0.3716-0.2
R1000 10.0 FISC
R1000 1.00 FISC
R1000 1.00 FISC
SPEED 500. (CP+)

* TIME 0.0 4.0 15 SEC

* RATE

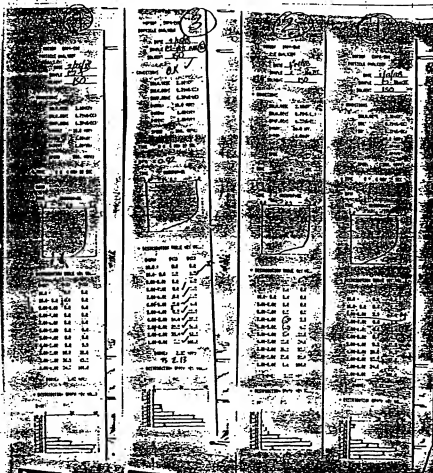


* DISTRIBUTION TABLE (BY VOL.)

D(P)	F(1)	F(2)
0.0-0.5	0.0	0.0
0.5-1.0	0.0	0.0
1.0-1.5	2.7	0.0
1.5-2.0	0.0	0.0
2.0-2.5	0.0	0.0
2.5-3.0	0.0	0.0
3.0-3.5	0.0	0.0
3.5-4.0	0.0	0.0
4.0-4.5	0.0	0.0
4.5-5.0	0.0	0.0
5.0-5.5	0.0	0.0
5.5-6.0	0.0	0.0
6.0-6.5	0.0	0.0
6.5-7.0	0.0	0.0
7.0-7.5	0.0	0.0
7.5-8.0	0.0	0.0
8.0-8.5	0.0	0.0
8.5-9.0	0.0	0.0
9.0-9.5	0.0	0.0
9.5-10.0	0.0	0.0

NOTE: 1.24 (P)

* DISTRIBUTION TABLE (BY VOL.)



C2 PSDS

- 1) C2 MILL PASS II
- 2) C2 \downarrow PASS III of $\frac{1}{2}$ of ①
- 3) C2 MILL PASS IV of other $\frac{1}{2}$ of ①
- ① fines from ①, ②, ③

④ 3rd MILLING PASS ineffective due to clogged bag
& powder charged channels

The above understood
and witnessed by

Date

and
by

Date

36 SrTiO_3 3/4 Synthesis IBM Technical Notebook
 (see Book III, page 27 for work-up)
 No comp. 692, 393

Prep:
 SrCO_3 tare 206.15
 50.00 g desired
 256.15
 256.15/6 actual wgt
 0.0 Δ
 TiO_2 27.062 desired
 283.212 desired
 283.22 actual wgt
 +0.01 Δ
 +0.01 scale replace
 ~0.0 Δ net

Transfer
 tare 89.20
 166.23 final wgt
 77.03+
 77.062 expected
 -0.03 g Δ 0.04

185.56 total pred. wgt top
 19.33 g top

theoretical expected 151.36 wgt top
 19.33
 170.69 wgt top

$14.87 + 62.16 = 77.03 \sim \text{correct}$

Pump @ 700C/hr to 150C \Rightarrow to temp ~ 3:25

0.39/150.97 (0.258% loss)

GROUND yld \Rightarrow 61.39/62.16 \Rightarrow 98.8%
 ~1% grinding loss

Clean X-RAY. M.O. 1 HOUR
 Syn PROJECT COMPLETE
 3/5

The above understood
 and witnessed by

Date

and
by

Date

IBM Technical Notebook

38 SrTiO_3 GB Doping

10g SrTiO_3 w/ 2 wt % B_2O_3 added

Sp. g - 8.8 mp, 820°C

10g + 0.2g $\text{B}_2\text{O}_3 \Rightarrow 10\text{g}$

0.2g A_2O 2.4g/cc Decomposes above 300°C

$\text{AgNO}_3 \Rightarrow$ mp 212°C bp 169.8749 mw

4.323g/cc

0.2g $\text{Ag}_2\text{O} \times \Rightarrow 231.7394$
169.8749 g/mw $\Rightarrow 0.733, 1.364$

0.2g $\text{Ag}_2\text{O} \times \frac{169.8749 \text{ g/mw}}{231.7394 \text{ g/mw}} = 0.1466 \approx 0.15\text{g}$ OK

0.2g $\text{AgNO}_3 \times 169.8749$ X2 = 0.29

$2 \text{AgNO}_3 \xrightarrow{\Delta} \text{Ag}_2\text{O} + 2\text{NO}_2 + \text{O}$

~~0.2g $\text{Ag}_2\text{O} \times \frac{231.7394 \text{ g/mw}}{169.8749 \text{ g/mw}} = 0.273\text{g}$ AgNO_3~~

IBM Technical Notebook

124500 Doped ST₁O₃ pellets

STA-1 3.10 0.581 0.196
1.476 0.498
3.0 0.525 0.178
1.334 0.452

STA-3 deformed, SAK polish
3.64 75.7
0.852 4.75 98.8
C.632

STA-2 3.25 0.581 0.208
1.476 0.521
3.14 0.525 0.185
1.334 0.470

3.65 75.9
0.891 4.78 99.4 ← polish
0.657

124500 STB-1 3.03 0.587 0.191
1.491 0.485
2.88 ← 2.92 0.599 0.174
(dup) 1.370 0.470 0.644

3.58 74.4
0.847 4.47 92.9

STB-2 3.17 0.586 0.197
1.488 0.500
3.03 ← 3.21 0.179
1.370 0.455

3.66 75.9
0.869(5) 4.52 94.1
0.671

1221000 STB-3 3.77 0.583 0.237
1.481 0.60
3.61 ← 3.74 0.534 0.216
deformed 1.366 0.549

3.66 76.1
1.03 4.55 94.6 ← polish
0.773

ST-D1 3.62 0.585 0.235 ^{univ}
1.486 0.597
3.60 ← 3.67 0.527 0.210
1.339 0.533

1.036 3.55 72.8
4.77 99.2 ← polish
0.7505

Comments - grown D₂ fairly consistent, even w/ pressure variation

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IBM Technical Notebook

DD-X 37/27000
 2.88 0.573 0.169 4.04 63.4%
 1.455 0.429 C.713
 2.83 0.508 0.144 93
 1.290 0.326 C.478

DD-Y 2.99 0.575 0.174 4.04 63.4%
 1.46(5) 0.442 0.740(5)
 2.93 0.509 0.149 92.4
 1.293 0.379 C.498

10°C/MIN. RAMP IN NEW Al_2O_3 CRUCIBLE ON FRESH DD powder.
 975°C for 2 HOURS { QUENCH. 20min O_2 purge.

The above understood
 and witnessed by

Date

and
for

Date

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DOI: 10.1002/anie.200500000
 FULL PAPER

DATE 6.03
SAMPLE 2721
SUBSTRAT ISO

• CONF-11106*

SOLV. VISE	2.75 (CST)
SOLV. DEN	6.79 (G/CM ³)
SAMP. DEN	0.8618 (G/CM ³)
Q(CAN)	10.6 (WTS)
Q(CAN)	1.06 (WTS)
Q(CAN)	1.62 (WTS)
SPEED	540 (RPM)

* TIME * to * FILE * SET

• **MYO**

TIME RESPONSE



* DISTRIBUTION TABLE (Cf. 96)

Price	Qty	Cost
11.00	10.0	11.0
10.00	9.5	10.5
9.00	9.0	9.0
8.00	7.0	5.6
7.00	6.0	4.2
6.00	5.0	3.0
5.00	4.0	2.0
4.00	3.0	1.2
3.00	2.0	0.6
2.00	1.0	0.2
1.00	0.0	0.0

* DISTRIBUTION STATEMENT (if any):



REF ID: A66666

DATE 3/2/09
SAMPLE 2/24
CAN WEIGHT 150

• [FBI Press Release](#)

SOLV. VISC	2.7916
SOLV. DENS	0.7916
SAMP. PEMS	6.0416
D(REF)	10.0 (17)
D(REF)	1.0017
D(REF)	1.0017
COEFF	546.000

* TYPE 6 0 4 8 16 6 0 0

• 50%

TIME	RESOURCE
------	----------



* AUSTRIAN 100.1 (5x 70)

DOSE	FCI ₁	FCI ₂
10.0-0	0.0	0.0
10.0-5.0	2.5	2.9
9.00-0.00	7.1	10.6
8.00-7.00	7.1	17.7
7.00-6.00	4.6	22.1
6.00-5.00	0.3	36.4
5.00-4.00	22.4	51.6
4.00-3.00	12.6	65.8
3.00-2.00	15.7	81.1
2.00-1.00	14.5	91.5
1.00-0.00	0.5	110.1

• **DISTRIBUTION** **GENE** **CC** **YAC**



POSTED: 09/04/2004
POSTED BY: [REDACTED]

DATE 2/24/88
SHEET C2-POL, B
SHEET 150

• **PREPARE**

SOLV.WISE	2.16009
SOLV.WERE	6.79067
SOMP.WERE	6.34067
DCRPA	16.8179
DCRNP	1.00179
DCRPT	1.00179
SPEED	506.000

• TIME 00:14 ETx 20 SEC

• 963

LINE PERSONNEL



* DISTRIBUTION TABLES OF

01%:	F(2)	0.1:
10.0-0	0.0	0.0
10.0-5.0	0.0	0.1
5.00-0.00	0.0	0.1
0.00-7.00	0.0	0.0
7.00-6.00	5.1	5.1
6.00-5.00	12.7	12.7
5.00-4.00	12.7	25.5
4.00-3.00	16	39.6
3.00-2.00	25.7	65.1
2.00-1.00	24.7	91.7
1.00-0.00	6.3	100.0

• DISTRIBUTION: FREE OF CHARGE



The above understood
and witnessed by

Date _____ and
by _____

Date _____

42

IBM Technical Notebook

3/15 DC batch II Si_3N_4

ju tar 206.11 (206, unstable
 $\frac{256.06(7)}{49.95} g$ loss 0.05 (0.1%) desired 50g

$\frac{27.06 \cdot 2}{283.122}$ target
 $\frac{283.13}{27.07}$ actual ✓
 $\frac{77.02}{+0.008}$ total

$\frac{88.34(5)}{77.02}$ Pt. guss time total above
 $\frac{165.36(7)}{165.34}$ expected comb. wgt ✓
 .03 g error max, ✓ OK. (0.04% error)

~184.54 (19.20 tons) ✓✓ expect ~154.0 w/out top

~~100~~ 150.15 after cooling!

3/16 4.20 < 100 mesh 59.85 g ✓

ST-D2 (2.9um) mII
 $\frac{3750}{3.04} / \frac{125,000}{0.583}$ 0.206 3.38 70.3 %
 1.481 0.523 0.900
 $\frac{3.017}{1.306}$ 0.514 0.181 4.90 1.02 %
 0.460 0.616

The above understood
 and witnessed by _____

Date _____

and
 by _____

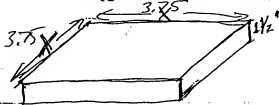
Date _____

7070 GLASS count

1 1/2"

7070 density - 2.13 g/cc $\Rightarrow \frac{\text{kg}}{1000 \text{ g}} \times \frac{0.00571 \text{ lb}}{3.23 \times 10^{-4} \text{ kg}} = \frac{0.00571 \text{ lb}}{\text{cc}}$

$0.00571 \frac{\text{lb}}{\text{cc}} \times 16.387 \frac{\text{cc}}{\text{in}^3} = 0.0936 \frac{\text{lb}}{\text{in}^3}$ tray conv.



$0.08 \times 0.08 \times 1.5 = 21.32 \text{ in}^3$

$\frac{21.32 \text{ in}^3}{24.9696} \times \frac{0.0001 \text{ lb}}{\text{in}^3} = 1.99 \text{ lb}$

$1.5 \times^2 (\frac{0.08 \text{ lb}}{\text{in}^3}) = 2$

$1.5 (0.08 \text{ lb/in}^3) \times^2 = 2 \text{ lb}$

$\$7.10^2$

$0.009 \times^2 = 2 \text{ lb}$

$x^2 = 18.86$

$x = 3.77 \approx 4.08$

check density conversion: $2.13 \frac{\text{g}}{\text{cc}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{3.15 \times 10^4 \text{ kg}}{\text{cc}} =$

OK

$\frac{0.00213 \text{ kg}}{\text{cc}} \times \frac{1 \text{ lb}}{0.435 \text{ kg}} = 0.0048965 \frac{\text{lb}}{\text{cc}}$

$1 \text{ lb} = 4.535 \times 10^{-4} \text{ kg}$
 $1 \text{ lb} = 0.435 \text{ kg}$

$0.0048965 \frac{\text{lb}}{\text{cc}} \times 16.387 \frac{\text{cc}}{\text{in}^3} = 0.08 \frac{\text{lb}}{\text{in}^3}$

$4 \times 4 \times 1.5$ or $5 \times 5 \times 1$

@ 1" thick $0.08 \times^2 = 2$
 $x^2 = 25$
 $x = 5$

IBM Technical Notebook

44

3/21 1st pellet 700C for 12 hrs → START @ 3 to ramp @
 10°/MIN) 50% 16-17 hrs.

C2P12 for green data on all pellets see pg 37

C2PB 2nd pellet 750C done to run concurrently

Peter,

Since we didn't get to discuss this experiment
 in more detail, here is what needs to happen.

5 pellets — C2
 1st) — 700° C ~12 hr α_2 308
 2nd) — 750° C ~12 hr α_2 302
 3rd) — 850° C " " 302
 4th) — 850° C " " "

After these intermediate temperature anneal,
 weigh and measure each pellet. If no sintering,
 or at least a negligible amount, has occurred, then
 re-fire each sample for 12 hrs again at the same
 intermediate temperature and then sinter each pellet
 for 2 hrs at 950°C. Ramp from the intermediate
 T to 950°C fast (~20°C/min).

Also sinter the 5th pellet at 950°C
 for 7 hrs, this is the control pellet. Thanks
 and have a good week.

Pierre

965C used

3/23 Temp raised to 950°C @ 9:00 AM
 to temp @ 9:15 AM

C2P12 3.06 ($\Delta=0.02$)
 3.01

0.572 0.191 no sintering, but 0.65% weight loss
 0.50 0.163 5.65
 1.27 0.414 0.533 88.7
 CRACKING = closing

C2P13 3.01 (0.05) ($\Delta=0.05$)
 2.97

0.572 0.187 no sintering, but 0.60% weight loss
 0.504 0.163 5.57 87.4
 1.280 0.414 0.533 NO CRACKING = open

The above understood
 and witnessed by

Date

and
 by

Date

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45

3/21 Sr.TiO₃ DRC batch 2 → fine coll after 3rd milling → 11g yield
after cleaning ~ 2g loss to machine
3g loss to blow-out
fines → 1.34 μm ave
medium III → ≥ 2.2 μm range (2.2-2.8)
approx. { 18% fines
82% medium
STDX 1f-1 0.570 0.212 3.09 6.42% SVEROS 72.3 μm probe
2.74 1.448 0.538(5) 0.887

In furnace ~ 3:00 p.m., tripped off @ 975 2X, cooled to 1400C, then to 1600C.
Temp. recovered / reset to 1650 @ 4:30 p.m.
3/22 RAN all NITE! 24 HRS @ 3:00 p.m. Tuesday, 42 HRS @ 9:00 a.m. Weds.
2.70 0.487 0.178 4.97 1.033% same as 2/21
1.237 0.452 0.543

Notes:
✓ ~~Start~~ Put, action and follow. Cu-Bi shot (Kurt Plan) start/finish 21/22
• Try firing one pellet of Sr.TiO₃ & 150C weight
• Try firing another pellet of Sr.TiO₃
→ Swabbed mill & TiO₂, probe down to 1/4 in. The mill
again "thru" the jet mill. Run at 150C weight
✓ • Mfr. note: batch of Sr.TiO₃?

tare 202.33 * approx. due to instability spans down: sometimes stable
DUCE
252.33 target
act weight 252.33 * 100
27.062
279.392
act weight 279.4 w/ 0.01
TRANSFER 165.22 act weight
tare 88.17
77.05 w/ 0.01 mix
77.07 expected
w/ 0.03% loss
POST/16HR 150.02
+ 19.87 g expected loss
164.89
15.2g actual loss

The above understood
and witnessed by

Date

and
by

Date

write-up 3/23, page 3/24

IBM Technical Notebook

46/3/22

C3-Synthesis
 (reference)

Synthesis
 BaCO_3

target $\rightarrow 277.72$ to zero

weight: $\frac{398.246}{120.52-54}$ total (-0.02%)

CaO

target $\rightarrow 0.89 \rightarrow$ zeroed
 weight: 72.58 (7/9) 3/23

transfused quat

CaO_2

target $\rightarrow 0.85 \rightarrow$ zeroed
 weight: 34.35 3/23

total expected $\Rightarrow 227.46$
 transfused quat, $+0.03\%$

Overwrite @ 70C w 30" vacuum after "lamp size" isopropanol mixing
 3/24 #1 cur $\frac{230.56}{116.57}$ #2 $\frac{230.41}{117.17}$
 $\frac{113.99}{113.24} \Rightarrow 227.23$ 0.1% loss or

Prior to removing from bkr after overwrite, capse broken up and
 pulverized, then let cool under vacuum to remove oxygen, reseed.

In Service @ 12:30 500C/hr RAMPs, 955 RWT in flowing oxygen
 POST $\frac{219.22}{102.65}$ $\frac{218.34}{101.17}$ $\Rightarrow 203.82$
 3/25 $\frac{101.79}{101.79}$ $\frac{100.74}{100.74} \Rightarrow 202.13$ 0.83% loss
 218.36

The above understood
 and witnessed by

Date

and
 by

3/8/71

Date

3/23 from pg 44 TREATMENT INQUIRY

47

C2P14 & C2P15 ⇒ original given info on pg 37; both 3.11 then

C2P14: (800°C pre-treat) page 2120 pm 59.9 ed. : 18 HRS
3.09 0.573 0.191 3.83 60.1 so appreciable sintering
1.455 0.485 0.806
3.07 0.512 0.171 5.125 80.5 apparently sintering
1.326 0.434 0.599 appreciable

C2P15: (850°C pre-treat) page 2120 pm 59.8 ed. : 18 HRS
3.09 0.565 0.187 4.02 63.1 slight amount of sintering
1.435 0.475 0.768
3.08 0.531 0.174 4.87 76.5% initial sintering "appreciable"
1.349 0.442 0.632

C2P18 (CONTROL) 37/27500
2.92 0.574 0.180 3.83 60.1% O.K.
1.458 0.457 0.763
2.86 0.501 0.152 5.82 91.4
3/28 1.273 0.386 0.491
Post 48 hr (2nd 24) - C3 batch

pre → 318.81
post → 316.88
1-1.83
302.13
200.30
199.23 initial yield

48/23 from page 45 IBM Technical Notebook

STD-1f grain size slightly larger - interior fairly uniform
 ~ 25 μ m away occasional

~~Re-sintered~~ Re-sintered overite to check for additional growth.
 further polishing of 40 hr sample slice yields numerous 40-50 μ m
 GRAINS. Growth seems prolonged

3/24 Summary from 45

Base: 2.74 1.448 0.538(5) 0.887

3.09 64.2

4.13 @ 2.70

1.237 0.452 0.543

4.97 100.33

1645C

slice back up to 1650 @ 5:00 PM (1 hr earlier due to control couple failure)
 63 HRS SHUT OFF @ 1:45 PM 3/24 (12.1 hr)

The above understood
 and witnessed by _____

Date

and

Date

3/24 from pg 45

after additional 12 hr rxn time $\frac{150.02}{149.81}$: Assume constant now

total loss: 165.22 initial 1 0.21 g
150.02 16 HR - 15.20 98.6% reacted
149.81 28 HR - .21 1.4%
15.41

CAUSE FOR MINOR porosity?

> 61 g recovered after mortar grinding.

> 2 HRS on shaker mill w/ 5mm balls.

> 60.4 g shaker yield

> 18.8 g MI JET YIELD

PSD
2.91 um ave. 1 Skitter
than jet, but not much
better for size.

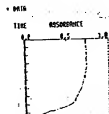
Slip-cast calculations: die 0.9" id. \Rightarrow 2.286 cm \uparrow 0.762 cm
0.3" desired green thick

$\frac{\pi \cdot (2.286)^2}{4} \cdot (0.762) = 3.1275 \text{ cc} \cdot (1.81 \text{ g/cc}) = 15 \text{ g SiTiO}_3 \cdot (0.6) = 9.0 \text{ g}$
approx density

50

IBM Technical Notebook

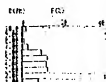
MODEL CPM-500
 PARTICLE ANALYZER
 DATE 5/18/68
 SAMPLE 5110-102
 SOLVENT MTH
 CONDITIONS
 SOLV. VISC. 2.10 CP
 SOLV. DENS. 0.7916 G/CC
 SHAP. DENS. 6.8116 G/CC
 CONDS. 10.0 CPM
 DENSITY 1.0000 G/CC
 DENSITY 1.0000 G/CC
 SPEED 500.0000
 TIME 0.0 4 SEC 0 SEC



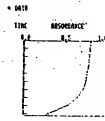
* DISTRIBUTION TABLE (BY VOL.)

CPM	FCI	FCI
10.0-5.0	0.0	0.0
10.0-5.1	0.0	0.0
5.00-4.00	0.0	0.0
0.00-7.00	0.0	0.0
7.00-6.00	0.0	0.0
6.00-5.00	0.0	0.0
5.00-4.00	0.0	0.0
4.00-3.00	0.0	0.0
3.00-2.00	0.0	0.0
2.00-1.00	0.0	0.0
1.00-0.00	0.0	0.0
DENSE	2.20	0.00

* DISTRIBUTION GRAPH (BY VOL.)



MODEL CPM-500
 PARTICLE ANALYZER
 DATE 5/18/68
 SAMPLE 5110-102
 SOLVENT MTH
 CONDITIONS
 SOLV. VISC. 2.10 CP
 SOLV. DENS. 0.7916 G/CC
 SHAP. DENS. 6.8116 G/CC
 CONDS. 10.0 CPM
 DENSITY 1.0000 G/CC
 DENSITY 1.0000 G/CC
 SPEED 500.0000
 TIME 0.0 4 SEC 0 SEC



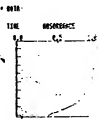
* DISTRIBUTION TABLE (BY VOL.)

CPM	FCI	FCI
10.0-5.0	0.0	0.0
10.0-5.1	0.0	0.0
5.00-4.00	0.0	0.0
0.00-7.00	0.0	0.0
7.00-6.00	0.0	0.0
6.00-5.00	0.0	0.0
5.00-4.00	0.0	0.0
4.00-3.00	0.0	0.0
3.00-2.00	0.0	0.0
2.00-1.00	0.0	0.0
1.00-0.00	0.0	0.0
DENSE	2.20	0.00

* DISTRIBUTION GRAPH (BY VOL.)



MODEL CPM-500
 PARTICLE ANALYZER
 DATE 5/18/68
 SAMPLE 5110-102
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 CONDITIONS
 SOLV. VISC. 2.10 CP
 SOLV. DENS. 0.7916 G/CC
 SHAP. DENS. 6.8116 G/CC
 CONDS. 10.0 CPM
 DENSITY 1.0000 G/CC
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 SPEED 500.0000
 TIME 0.0 4 SEC 0 SEC



* DISTRIBUTION TABLE (BY VOL.)

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10.0-5.0	0.0	0.0
10.0-5.1	0.0	0.0
5.00-4.00	0.0	0.0
0.00-7.00	0.0	0.0
7.00-6.00	0.0	0.0
6.00-5.00	0.0	0.0
5.00-4.00	0.0	0.0
4.00-3.00	0.0	0.0
3.00-2.00	0.0	0.0
2.00-1.00	0.0	0.0
1.00-0.00	0.0	0.0
DENSE	2.20	0.00

* DISTRIBUTION GRAPH (BY VOL.)



MODEL CPM-500
 PARTICLE ANALYZER
 DATE 5/18/68
 SAMPLE 5110-102
 SOLVENT MTH
 CONDITIONS
 SOLV. VISC. 2.10 CP
 SOLV. DENS. 0.7916 G/CC
 SHAP. DENS. 6.8116 G/CC
 CONDS. 10.0 CPM
 DENSITY 1.0000 G/CC
 DENSITY 1.0000 G/CC
 SPEED 500.0000
 TIME 0.0 4 SEC 0 SEC



* DISTRIBUTION TABLE (BY VOL.)

CPM	FCI	FCI
10.0-5.0	0.0	0.0
10.0-5.1	0.0	0.0
5.00-4.00	0.0	0.0
0.00-7.00	0.0	0.0
7.00-6.00	0.0	0.0
6.00-5.00	0.0	0.0
5.00-4.00	0.0	0.0
4.00-3.00	0.0	0.0
3.00-2.00	0.0	0.0
2.00-1.00	0.0	0.0
1.00-0.00	0.0	0.0
DENSE	2.20	0.00

* DISTRIBUTION GRAPH (BY VOL.)



The above understood

Date

and

Date

IBM Technical Notebook

51

3/7/93

10g $\text{SrCO}_3 \Rightarrow 0.06774$ moles
5.412g TiO_2

15.412g total

15.48 after mixing ~~15.48~~

Dave's unreacted $\text{SrCO}_3/\text{TiO}_2$ { new batch SrTiO_3 }

2.975 0.584 0.242

2.42 0.458 0.190
1.16 0.483 0.510

(4.745)

(98.6)

NOT TOO GOOD

⊗ 2.91 0.585 0.194

2.90 0.488 0.173
1.326 0.439 0.606

(4.785)

(99.5)

NOT TOO GOOD

3/25/93 Note
Density calculations here
were done using ρ_{TiO_2} lit.
which is now known to be in
error. It is 5.116 not 4.82

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 Register with Local Recorder

Disclose in every entry. Have every possibly important
 idea recorded. Submit an Invention Disclosure of
 as possibly new and inventive.

52.4/1 ~~STiO₂~~ *grow growth* IBM Technical Notebook

pellets of fines

2.22	0.592	0.169	3.12	64.9%	<i>as shown as before</i>
	1.453	0.429	0.711		
2.19	0.487	0.144	4.98	<u>10035%</u> = 103.5	
	1.237	0.366	0.640		

2.71	0.580	0.176	3.96	74.0%
Dunes Xcess	1.473	0.447	0.762	
TiO₂				
<i>estimate on 1/2</i>	0.518	<i>(0.262) 0.16 C</i>	4.86	<u>→ 1.01</u>
<i>etc 35</i>	1.32	0.406	0.556	101.-
<i>(2.70)</i>	1.32	0.406		
<i>~ O.K. by wght.</i>				

The above understood

Date

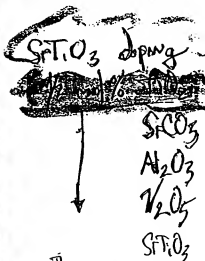
and

Date

IBM Technical Notebook

M.W.

53



X2
0.0679 0.135225g batches
excess 0.125 0.25
STOIC as nitrate
0.036 0.072
0.1754 0.308

79.90

0.0676

147.63

101.96

181.88 3337 690C

183.5182

13.531 TiO₂ 0.16935 moles 0.00084675 = 1/2 mole %
25.00 SrCO₃
38.531

$$0.00084675 \text{ moles } (79.90) \rightarrow -0.06766 + 13.531 = 13.46$$

$$0.00084675 (147.63) \rightarrow -0.125 + 25. = 24.875$$

Summary of additions, quantities

	excess	SUBZ 1	SUBZ 2	excess 2
TiO ₂ 2	13.5986	13.443	13.321	13.598
x2 SrCO ₃	25.00	25.00	24.875	25.225
x2 Al ₂ O ₃	-	0.086*	-	-
V ₂ O ₅	-	-	0.154*	-

* these quants are X2 since there are 2 moles of Al { 1/10 Al₂O₃ } { 1/2 V₂O₅ }

Correction: $\frac{0.16}{147.63} = 0.00108 \text{ moles SrCO}_3$

$\frac{0.00108 \text{ moles}}{0.00167}$ { 64% with loss due to decanting approx }
70% stoic or 30% off addition excess
V₂O₅

The above understood and witnessed by

Date

and by

Date

IBM Technical Notebook

54 4/5

Sub2 72.05 1 mol % stoichiometric / net excess (see pg 53)

25.0 g SrCO_3 weighed & transferred to beaker
 0.16 g removed
 0.16 g V_2O_5 added (1.20% saturated) in hot water, decont'd)

MISTAKE, now uncorrectable. Should have been:

$$0.00084675 (2) = 0.0016935 \text{ g } \text{SrCO}_3 \text{ removed}$$

0.0016935 (147.63) = 0.25 g however, deconting over
 residual pack reduced actual V_2O_5 addition, and though
 NONSTOICHIOMETRIC (slightly) will use to see what happens.

38.62 g yield after overide vac. @ ~90°C
38.53 initial
 0.51 loss in mixing 1.3 %

38.88 tare (zeroed)
38.08 406 error due to final beaker scrape ✓

In furnace to temp by 12:00, 4/6/88 16 HRS 8 P.M. 4/7
 'Severe' sintering, dark black appearance of pack body

126.96
 117.68
 ~ 9.28 g spillage

25g $\text{SrCO}_3 \times \frac{147.63}{147.63} = 17.55$

126.96
 117.73

126.96
 117.68

~ 7.40 g expected loss

9.28

! some bound water?

26.18 g ground yield

57 58
 59 ENTERED

The above understood
 and witnessed by _____

Date

and
 by

Date

IBM Technical Notebook

Sub 1 ~~Al₂O₃~~ → 1 mol % added as nitrate

$$0.0028475(2) = 0.0016935 \text{ moles} // \text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} \quad 375.14$$

\downarrow 1/2 mol % 1 mol % Al 1:1 so use 0.0016935 moles

$$0.0016935 \text{ moles Al nitrate} \left(\frac{375.14 \text{ g}}{\text{mole}} \right) = 0.6353 \text{ g}$$

(303142)

So remove 0.0016935 moles TiO₂ ∴ 0.0016935(79.9) = 0.135 g TiO₂

$$\begin{array}{r} 13.531 \\ - 0.135 \\ \hline 13.396 \text{ g TiO}_2, 0.6353 \text{ g Al nitrate in soln} \end{array}$$

$$\begin{array}{r} 38.29 \text{ max yield} \\ 39.03 \text{ theoretical} \\ \hline 0.74 \text{ max loss} \end{array} \quad 1.9\%$$

$$0.6353 \text{ g} \left(\frac{101.9612}{375.14} \right) = 0.173 - \Delta 0.16$$

$$\begin{array}{r} 39.03 \\ - 0.96 \\ \hline 38.07 \end{array}$$

87.55 tare (weighed) 38.27 net ⇒ 0.3⁺ max loss ✓
 note: nitrate decomposes in hot water. Must explain some of loss

In furnace to temp by 12:00 p.m., 4/6/88 ⇒ 16 hrs 8 am 4/7
 Little sintering of powder, light SrTiO₃ color, mottled.

$$\begin{array}{r} 118.54 \\ 127.82 \\ \hline - 9.28 \text{ g} \end{array}$$

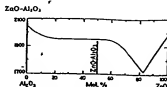
same as SUB 2! behaving the same, even though exact loss is coincidence

yield → 27 g

see 57 } 58
 for SINTERED DATA
 Date

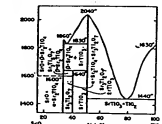
119

Figs. 295-301



For 196.—System 50-50.
F. Reiche, *Ann. J. Sci. Sch. Ser.*, 4, 336 (1922); modified
by J. W. Giese, *ibid.*, Sch. Ser., 13, 19 (1927); see also F.
C. Knecht, *J. Am. Chem. Soc.*, 52 [4] 1440 (1930).

FIG. 219.—Liquidus curve of system $\text{ZnO}-\text{Al}_2\text{O}_3$.
J. N. Bunting, *Bur. Standards J. Research*, 9 [1] 280
1922; R. F. 412.

 $\text{ZnO-B}_2\text{O}_3$ 

Feb. 297.—System SrO-TiO_2 .
Miroslawa Dryl and Włodzisław Trzebiński, *Rachunki Chem.* 31, 492 (1957).

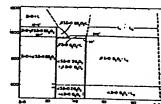
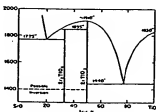


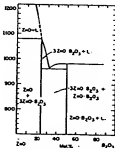
FIG. 300.—System $\text{ZnO}-\text{B}_2\text{O}_3$.

D. E. Harrison and F. A. Hummel, *J. Electrochem. Soc.*, 103 (9) 490 (1956); see also, "Structure of Zinc Metaborate, $\text{Zn}(\text{BO}_3)_2$," P. Smith, S. Corbin-Blanco, and L. Kevais, *Anales Real Soc. Espan. Fis. Quim. (Madrid) Ser. A (Nouv. Ser.)*, 203-208 (1961).

Miroslawa Dryl and Wladyslaw Truchniewski
Chim., 31, 422 (1957).



Foot. 208.—System S-O-TIO; tentative.
Reston Key; private communication. 103]



Yu. S. Lomonosov, *Zhur. Neorg. Khim.*, **3**, 1746 (1958)

Two Oxidizers

Fig. 104-2338

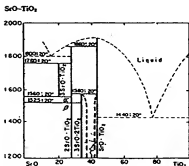
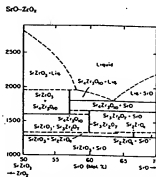


Fig. 2334.—System SrO-TiO_2 . SrO-3TiO_2 is extended to approximately the SrO:TiO_2 composition.

Antonio Cecce and Frances Monahan, *Ann. Chim. (Rome)*, 53, 897 (1963).



Fel. 2331.—System $\text{SrO}-\text{SrZrO}_3$.
Gilbert Tilley and Monique Percey y Jorda, *En. Hando*
Temp. Refractivity, 1 [4] 237 (1964).

Gilbert Tillack and Manique Perez y Jurba, *En: Hacia Temp. Refractores*, 1 (4) 237 (1964).

Those Diagrams
(arrows)
for $\text{SrO} \cdot \text{TiO}_2$
system and
associated others

The above understood

Date and

Date _____

Excess SrTiO_3

(Excess 2) IBM Technical Notebook

(Excess 1)

57

13.531 TiO_2
13.53-

25.25 SrTiO_3
25.28

13.6 TiO_2
13.61

25.00 Sr
25.02
.03 to

2000 off after addition
probably static

In drying oven @ ~100C under house vacuum @ 1:30 p.m. 4/6/61

38.72 after drying
87.87 weighed crucible
126.59 w/ addition
118.85
7.74

38.48 after drying
87.07
125.50
117.99
7.71

25 g x $\frac{101.96}{375.14} = 6.715$ 17.5

$\frac{6.715}{7.74} = 86.87\%$ 12% excess loss
7.5 / 7.74 = 97.5% +

#1 $\leftarrow \text{TiO}_2$

#2 $\leftarrow \text{SrCO}_3$

NO GREEN DATA TAKEN

NO GREEN DATA

2.75 0.520 0.159
1.321 0.404 0.554
N₂ 2.71 0.529 0.160
1.344 0.406 0.576

4.96 1.03 3.01 0.517 0.175 5.0 1.04
EXCHANGE 1.313 0.444(5) 0.60
4.71 97.4 3.00 0.520 0.176 4.89 1.02
1.321 0.447 0.613

SrB₂
2.38 0.540 0.135 4.69 97.5
1.372 0.343 0.507
N₂ 2.41 0.554 0.141 4.31 89.6
1.410 0.358 0.559

SrB₂
2.56 0.529 0.150 4.74 98.1
1.344 0.381 0.5405
2.60 0.526 0.151 4.83 1.00
1.336 0.384 0.538

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IBM Technical Notebook

SUBSTITUTION 1: Al_2O_3 1 mol % 16 HRS. BAK

" 2: Y_2O_3 ↓

N_2 O_2

1: 100.4 98.5

2: 89.6 97.5

EXCESS DOPING 1: Y_2O_3 1 mol % TiO_2

" 2: ↓ $SiCO_2$

N_2 O_2

1: 97.4 103

2: 102 109

MECHANICAL MANIPULATION

finer : 103.4

finer $1/3$, med $2/3$ mix : 102.3

MED : 100.4

The above understood

Date

and

Date

4/11 Phase Co/Bi studies IBM Technical Notebook

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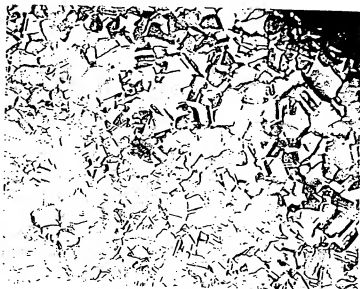
600C overnite N_2 treatment on as rec'd material (Cu)



INTERIOR
INHOMOGENEOUS
(ABNORMAL)
GRAIN GROWTH

100X

100 μm



EXTERIOR
INHOMOGENEOUS

100 μm

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Date _____

and
by _____

Date _____

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IBM Technical Notebook

1, 3, 10% Bi in copper

5g total per batch

4.95 post 750C

$g\text{ Bi} : 5(0.01) = 0.05 \quad 5(0.03) = 0.15 \quad 5(0.10) = 0.5g$

$Cu \quad \underline{4.95} \quad \underline{4.85} \quad \underline{4.50}$

actual $0.05-6 \quad 0.15-0.16 \quad 0.50-1$

$4.95-6 \quad 5.00 \quad 4.99-5.0$

recovery $4.87 \quad 4.99 - \quad 4.95$

$5.00 \quad 4.98 \text{ after 400C over (not standard)} \quad 4.90 \text{ after 400C overwrite}$

Reloaded 1% $\frac{1}{2}$ will continue w/ 3%. Will make a new 10%
 and a 50% and fire @ 750C. Crucible shortage \rightarrow will likely
 modify above.

50/50

2.5g Bi, 2.5g Cu

10%Bi

3% as above

$g\text{ Bi} : 2.51 \text{ actual}$

$post\ Cu \quad \underline{5.01}$

$Cu \quad 2.40$

Post 750C

$1.34 \quad 6.34 \quad 5.00 \quad 4.91$

$0.51 \quad 5.02(3) \text{ total} \quad \underline{4.51(2)}$

Post 750C

$1.32(3) \quad 6.24 \quad 5.00 ? \quad 4.92$

$6.21 \quad 4.89$

400C RESULT

NOTE: INITIAL 400C (420C) below (1-10%) percentages of Bi
 did not produce expected densification/solidification of peaks.

The above understood

Date

and

Date

IBM Technical Notebook

61

D5 { 35% Bi/Cu melts & 1 Bi crucible filling

25%

$$0.028(5) = 1.25 \text{ g Bi}, 3.75 \text{ Cu}$$

6.33 PRE

$$\frac{1.33}{5.00}$$

1.75 Bi ; 3.25 Cu

6.25(4) loaded

1.30(1)

4.95 starting total

6.30 post $\Delta = 0.03$
Possible post density: 0.315, 0.385
4.97 0.800 0.978 0.6

6.23 $\Delta = -0.02$

90
definitely smaller volume, higher density

4/16 Argon/H₂ Bi filling

13.32 post

2.21 PRE

13.18

11.86

0.148

13.30 after slag removal

25%

1.26 Bi

5.03 Cu

solid 12.82
cruc: 11.39(40)
11.43

CRUX \Rightarrow

post 12.81

ARGON/H₂ 25% Bi Run \leftarrow Pellet Run \rightarrow

pellet: 4.87 0.485 0.222
1.232 0.564 0.672

7.25 79%

$$8.96 \times 0.75 + 0.25(9.8) =$$

$$9.8 + 6.72 + 2.45 = 9.17$$

French started 2HR purge 3:35 "1" to Bi vaporization 3"
4.84 0.485 0.234 2nd pellet bloating do to Bi vaporization 3"

Bi₂O₃: sp. g. 8.8 m.p. 820°C

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IBM Technical Notebook

SnTiO_3 Grain Growth Experiment - MECHANICAL MEASURES

- 1) PSD weighting
- 2) fines full density & free sintering of polished surface
- 3) reacted to constant weight (1st batch) sintering as in #2

SINES = F

2.04	0.570	0.155		3.14	65.3
	1.498	0.374	0.649		
2.01	0.488	0.132		4.975	102.4
	1.239(5)	0.335	0.409		

fines/median = FM

2.19	0.577	0.154		3.32	69.0
	1.465	0.371	0.659		
2.17	0.504	0.135		4.92	102.3
	1.28	0.343	0.441		

2.46(7) μ	0.582	0.165		3.43(5)	71.4
	1.478	0.419	0.719		
2.46*	0.589	0.147		4.85	100.4
	1.318	0.373	0.509		

REMARKS \rightarrow * some powder adhered

IBM Technical Notebook

4-12-88⁶³

Switcing Regime

Rapid Temp w/ 10 cc/min O₂

4:25 p.m.

1550C. initial set, after REACHING temp for 1 hr, 1640C overnite

5:20 p.m. ~ 1100C, Tempura blown. @ ~ 30-45 minutes @ 1540.

Restarted @ ~ 5:55 f. brought directly to 1640C.

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and
by _____

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IBM Technical Notebook

64-26-88

LEAK TESTING: - SCOTTOR HIGH VAC

25 millitor after continued pumping through system
STARTING WITH Roughing - rate

Will close pumpdown through HVAC valve alone
tomorrow.

4/27 - Vacation

4/28 Pump down through high vac, initially unsuccessful, must
have been stuck valve, but after fix, we can get down
to ~50 millitor in 15 minutes. Will continue pumping.

1/2 40

Down to 10 thru rough, 30 w/ HVAC only.
Rather quick leak-back when both closed off indicating
leaks in system.

- 1) Furnace
- 2) Elbow connection
- 3) Pump

see page 78

5/13 Promised CSS test Monday (check!)

5/13

First Milling - AutoSeed - Teflon liner (13)

48.17 g known, but "few" voids before total process weight. checks

49.69 g yield

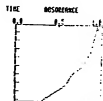
UNITED CAP-SEC
PARTICLE ANALYZER
DATE 5/13
ANALYST SAMPLE CS-200-1
SOLVENT ISO
Teflon liner

CONDITIONS
SOLV. WISC 2.100P
SOLV. WISC 0.750P/L
SOLV. WISC 4.300P/L
SOLV. WISC 10.400P/L
SOLV. WISC 1.000P/L
SOLV. WISC 1.000P/L
SOLV. WISC 1.000P/L
SOLV. WISC 1.000P/L

SPEED 500 (PPH)

* TIME 0.0 4.0 20.0 SEC

* DATE

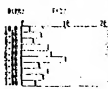


* DISTRIBUTION TABLE (BY VOL. %)

WGT.	WGT.	WGT.
10.0-5.0	49.7	49.7
10.0-5.0	1.0	50.6
5.00-4.00	4.5	54.1
4.00-3.00	2.7	56.8
3.00-2.00	6.1	62.9
2.00-1.00	6.9	69.7
1.00-0.00	10.2	80.0
0.00-0.00	4.0	84.0
0.00-0.00	6.0	90.0
0.00-0.00	5.0	95.0
0.00-0.00	3.2	98.2

SCHEMATIC 5.00 (PPH)

* DISTRIBUTION GRAPH (BY VOL. %)



The above was witnessed by

PASS II 5/16

47.6 g yield: much fluffier, looks ~ like 3um powder.

IMMEDIATELY RE-MILLING

pg 66 for PSD sheets ~ 2g loss

PASS III 45.8
45.8

PASS IV 44.5
~ 18.0 5 pellets
26.5

High large particle % 41.7 vs 18 for C2

overall ave. ~ 10 vs 5-6 for C2

however distribution seems similar { some bypassing must have occurred.

Will work on Tuesday.

Date

and by

Date

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ssibly new and inventive.

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67

B₁/C₀ 25/75 ~~grainy, packed~~, sinter overnite in Ar/H₂ (5)
@ 750°C.

#1 → < 100 mesh Cu, spherical (new)

#2 → ^{10 μm} ~~100 mesh~~ spherical Cu (old)

#3 → penetration
10 μm spherical

#2: 1.25/5.01
6.34
cew 1.34
5.00

#1: 1.25/5.00
6.35
1.35
5.00

POST. 6.31

6.32

8.0-8.5 mm l

8.37

9.65-9.75 mm dia

9.65-10.0

After interruptions: 5/24/ start cut { polystyrene
6/8/88 finish: 6/8/88 after

{ Porosity is reduced, and ^{3rd} 'oxide' has been eliminated }
in forming gas. (grey)

68 C3- P1-5 Green Data IBM Technical Notebook
iso 275 G mm mm Sinter
C3P1 3.59 1.470 0.774 0.80 70.5
3.33
C3P2 3.33 1.477 0.442 0.757 4.40 69%
2.93
C3P3 3.58 1.472 0.478 0.813 4.40 69%
C3P4 3.37 1.476 0.440
C3P5 3.53 1.474 0.471 5.52 87 even w/ working
3.19! 1.331 0.415 0.577 pure OK. I think
Mill no good.

NOTES: PELLETS SEEM TO HAVE SHED ORGANIC/GAS?!
looks like the pellet melted in plastic container.
ISO 26 UNIC 6200 20/→ 350, 10/→ 475, 24RS,
C3P6 2.52 1.50 0.32 4.46 70.1%
Course 2.50 1.482 0.316 4.55 71%
0.55

Calcinations - 750C IBM Technical Notebook
IN @ 8:00 P.M. 5/17/88 sat 9:00 5/18 69

TiO₂ - Cnec 395

$$\begin{array}{r} 16.3620 \\ - 0.8610 \\ \hline 15.501 \text{ g TiO}_2 \text{ weighed} \end{array}$$

$$\begin{array}{r} 89.4610 \text{ cwx} \\ 105.0174 \text{ cwx + TiO}_2 \end{array}$$

15.5564 g TiO₂ by difference

$$\begin{array}{r} 5/18 \text{ POST} \\ 105.0174 \\ 104.9395 \\ \hline 0.0779 \end{array} \text{ gaining } \Delta T > \Delta T_{\text{CO}_2}$$

$$15.501 = 0.5\% +$$

$$\begin{array}{r} EQ \rightarrow 105.0094 \\ 105.0174 \\ \hline 0.0090 \end{array} \text{ } 0.0090 / 0.0779 = 88.5\% \text{ bal}$$

$$99.64\% \rightarrow 0.3\% \Delta + 0.0554$$

SiCO₃

$$\begin{array}{r} 18.4193 \\ 0.8740 \\ \hline 17.5473 \end{array} \rightarrow \begin{array}{r} 0.8732 \\ 17.5441 \end{array}$$

$$\Delta 0.0032 \approx \Delta \Delta D.S. !!$$

$$\begin{array}{r} 109.9615 \\ 92.3660 \\ \hline 17.5955 \end{array} \Delta + 0.0514$$

$$\Delta \Delta D.S. \Rightarrow 0.004 \text{ g} \sim 4 \text{ mg} \text{ calibrate}$$

$$\begin{array}{r} \text{POST } 109.9615 \\ 109.8870 \\ \hline 0.0745 \end{array} \text{ } 0.0745 / 17.5441 = 0.4\%$$

$$\begin{array}{r} EQ \quad 109.9510 \\ 109.9615 \\ \hline 0.0105 \end{array} \text{ } 85.6\% \text{ back}$$

5/19 TiO₂ { ~~SiCO₃~~ 2nd CO₂ POST

$$\begin{array}{r} 105.0174 \\ 104.8670 \\ \hline 0.15 \end{array} \text{ } (-0.0003 \text{ cal})$$

$$\sim 1.1\%$$

$$\begin{array}{r} \text{SiCO}_3 \\ 109.9615 \\ 109.8580 \\ \hline 0.1035 \end{array} \text{ } (-0.0003 \text{ cal})$$

$$\sim 0.6\%$$

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HF Silicon Etch/Wash/Buffer Solns.

$\left\{ 80g \text{ NH}_4\text{F} \text{ in } 120g \text{ H}_2\text{O} (\text{Soluble}) \rightarrow \sim 120 \text{ cc } 40 \text{ wt. \% NH}_4\text{F} \right.$
REAGENT

actual soln is 40:1 ~~10:1~~ $\sim 170 \text{ cc}$

BHF \rightarrow 40 parts NH_4F reagent : 1 part HF (49 wt%) soln.

QUENCH \rightarrow 10:1 DI : NH_4OH reagent 50ml:500ml

BHF clean \rightarrow 10:1:2.2 ($\text{NH}_4\text{F}:\text{HF}:\text{Glycerin}$)
reagent 49

$16(10) = 160$ $16(1) = 16$ $16(2.2) = 35.2 = 211 \text{ ml}$
320
350
(190) (35) (27)

MSG:FROM: SARDESAT--FSHVNCC TO: NDT --YKIVMT

05/18/88 12:39:40

From: Vira) Sardesai
8-533-8545, SCL Pers Metals, GTD E. Fishkill
IBM INTERNAL USE ONLY (Unless otherwise specified)
SUBJECT: BHF concentrations used in SCL

Michael,

We use 40:1 BHF for pre platinum, emitter screen ox removal and for s metal
preclean.

The chemical is commercially available premixed solution and has 40 parts (by
volume) of 40 wt pct NH4F solution mixed with 1 part of 49 wt pct HF solution.
Both NH4F and HF are in aqueous solutions. Manufacturer specs the HF concentra-
tion to 0.61 to 0.77 moles per liter and specific gravity of 1.106.

For 5 postL/O BHF clean 10:1:2.2 (NH4F:HF:Glycerin) is used prepared
similarly and quenched in 10:1 NH4OH solution (28 wt pct NH4OH solution
diluted 10 times its volume in DI water).

cc: SZECST --FSHVNCC

HOUGHTON--FSHVNCC

Regards,

VIRAJ

FSHVNCC(SARDESAT), D/116 B/322 Z/571

***** OUR TEAMWORK MAKES THE DIFFERENCE ! *****

BHF concentrations used in SCL

BHF

BHF CLEAN

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IBM Technical Notebook

- mill #2

73

5/18 Polymilling

40g batch yield

I

36.8

PSD 1 2 Δ

6.94 4.84 3

II

33.4

3.65 3.21 3

III

31.3

8.53

(2) big change required

IV

28.4

2.98!

3 actually higher erroneous 7% @ 7.

V

25.75

3.1!

2.5 new log

DO

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and
by _____

Date _____

ISO 28,

74

IBM Technical Notebook

MARIONAL GREGG
 DENSITIES

CSP6	3.29	1.474	0.471		4.11	64.6
	3.23	1.343	0.416	0.80	5.48	86.2 !
				0.59		
CSP7	3.19	1.476	0.455		4.00	64.5
	3.13	1.343	0.404	0.779	5.49	86.3
				0.57		
CSP8	3.21	1.473	0.462	0.787		64.1
	3.16	1.341	0.409	0.577	5.48	86.2
						} TO KING-TU.
CSP9	3.08	1.474	0.441		4.09	64.3
	3.02	1.336	0.391	0.7525	5.51	86.6
				0.548		

NOTES: PELLETS W @ 4:55 with flowing O_2 (bottled, dessicated)
 Heating started @ 5:15 @ 20°/min (97°C @ start)
 @ 265°C cut back to 10°/min; to reach sinker T_i @ 6:35 pm.
 Starting @ 975°C for 2 HRS. till 8:35 pm.
 Quench } remove.

IBM Technical Notebook

75

995C sister
 CSP10 3.18 1.474 0.453 4.114 64.7
 3.11 1.338 0.399 0.773cc 5.54 87.2
 0.561

no (appreciable) loss!

13 "leg"
 yield Press Δ → Mill #1
 10.35 0

fine pat dia.
 <100 mesh

29.~ I 10 ! 12g leaks 3.29
 21.5 II 8 ! ~1g leak 3.11
 18.5 III 3 ! 4.0⁺ g of ~2.0um powder in mill neck

22.4 total mix yield

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"T3" pellets IBM Technical Notebook

C3P10-18
P15C
C3P10 ① 3.14 1.461 0.473 3.975 62.60
✓ 3.08 1.304 0.400 0.79 5.75 90.4
0.536

C3P12 ② 3.28 1.462 0.495
C ✓ 3.21 1.308 0.417 0.56 5.73 90.0

C3P12 ③ 3.04 1.463 0.450
2.97 1.307 0.388 0.54 5.68 89.31
1.310 0.385 0.523 5.756 90.5
1.306 0.516

C3P14 3.21 1.464 0.473
✓ 3.14 1.308 0.405 5.77-8 90.7-9
1.306 0.548

1000C
C3P14 3.04 1.461 0.452
2.97 1.298 0.386 5.81 91.35
0.511

C3P16 (pellets) 3.08 1.466 0.457
3.02 1.301 0.390 5.82 91.5
0.519

C3P17 3.28 1.464 0.492 5.75 90.4
3.22 1.298 0.422 0.568 5.82 91.5
(3.28) chip off

78. 6/8/88

IBM Technical Notebook

Centorr HVAC system close to finished with leak testing,
preliminary operation checks.

System mechanical pump down < 20-30 minutes

Torbon molecule \downarrow down \rightarrow to 5×10^{-5} within 1 hr
with attachments at mid 6th by 1:00 p.m.
Start was 9:15 originally.

Block-off flange, new Centorr purge / plug fittings still
needed. Failure leak test reg.

IBM Technical Notebook

Bi/Cu Free-Runable Sinter Vacuum Run

To glass shop 6/7/88. Batch size to be 4.0 g to allow for ease of manipulation during sealing of quartz tube.

$$4.0 (0.25) = 1.00 \text{ g Bi}$$

$$\downarrow (0.75) = 3.00 \text{ g Cu (will use 10 \mu m Cu powder)}$$

$$\begin{array}{rcl} \text{Bi} & \rightarrow & 1.00 (0.99) \\ \text{Cu to} & & 4.03 \\ \text{Cu} & & 3.03 \end{array}$$

$$\text{from JAR } 2.02 (1)$$

$$\begin{array}{rcl} \text{max} & & 1.83 \\ \text{w/ mix} & & 5.33 (4) \\ & & 4.00 (1) \\ & & 4.01 \end{array}$$

$$\begin{array}{rcl} \sim 24.8\% & \sim 25\% \\ 75.2\% & 75\% \end{array}$$

Redo - spilled in glass shop

6/9 New crucible shape/size for stability

lets take 5.0 g batch

$$1.25/5.0 (\pm 0.01)$$

$$\begin{array}{rcl} \text{crucible} & & 3.35 \\ \text{w/ mix} & & 8.35 \\ & & 5.00 \end{array}$$

6/14 After overnight sinter & removal from quartz tube

conc. of sinter 8.30 g (some spillage w/ tube before heat treatment)

no appreciable vapor product seen

Conclusions: Vacuum doesn't appear to work as well as Ar/H₂. Sample full of holes, but no evidence of oxidation, so holes are real. Again, no evidence of vapor phase deposition in tube.

IBM Technical Notebook

80 6/14/88

To do: 10, 20, 25 % in Ar/H₂ (9)

MONDAY (VACATION)

WENDS 6/22/88

RUN!

5 gram batches: 0.25 (5) = 1.25 B. / 3.75 C.
0.20 (5) = 1.00 B. / 4.00 C.
0.10 (5) = .5 B. / 4.5 C.

I
II
III

POUR (D)
I
II
III

BATCH ORDER

I 5 gram w/ new conical crucible

mix 9.03

tare 1.03

5.00

PRE

voids, but some areas seem OK.
has small voids, some good regions - voids (II)
however large voids & my string. Not
repeating, maybe longer times.

II

9.00

tare 4.00

5.00

seems very good, no large voids, mix very well.
microscopic exam shows many small pockets
or voids. Usually circular

III

6.31

tare 1.31

-5.00 'normal loss, possible'

did not densify fully

SCTD, Milling Results

MOPRO CPM-500

PARTICLE ANALYZER

DATE 7/24/68
 SAMPLE SCTD-150
 SOLVENT MT-MED

* CONDITIONS

SIGHT MODERATE
 SOLV. VISC 2.10 CP
 SOLV. DENS 0.794 G/CC
 SHAP. FENS 0.816 G/CC
 D (MM) 16.6 UPT
 D (P) 1.00 UPT
 D (T) 1.00 UPT

SPEED 500. UPT

* TIME 0.0 6.0 12.0 SEC

* DATE 7-03

TIME RESPONSE



* DISTRIBUTION TABLE (BY VOL.)

CPM	F12	F122
10.0-6.0	0.0	0.0
10.0-5.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	2.0	2.0
7.00-6.00	4.4	0.4
6.00-5.00	8.5	12.2
5.00-4.00	11.1	34.2
4.00-3.00	11.1	45.4
3.00-2.00	22.6	67.4
2.00-1.00	22.6	85.1
1.00-0.00	14.2	100.0

D (MM) 2.75 UPT

* DISTRIBUTION GRAPH (BY VOL.)



MOPRO CPM-500

PARTICLE ANALYZER

DATE 7/24/68
 SAMPLE SCTD-150
 SOLVENT MT-MED

* CONDITIONS

SOLV. VISC 2.10 CP
 SOLV. DENS 0.794 G/CC
 SHAP. FENS 0.816 G/CC
 D (MM) 16.6 UPT
 D (P) 1.00 UPT
 D (T) 1.00 UPT

SPEED 500. UPT

* TIME 0.0 6.0 12.0 SEC

* DATE

TIME RESPONSE



* DISTRIBUTION TABLE (BY VOL.)

CPM	F12	F122
10.0-6.0	0.0	0.0
10.0-5.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	0.0	0.0
7.00-6.00	0.0	0.0
6.00-5.00	0.0	0.0
5.00-4.00	0.0	0.0
4.00-3.00	5.0	7.4
3.00-2.00	12.4	22.6
2.00-1.00	41.0	64.2
1.00-0.00	32.5	100.0

D (MM) 1.34 UPT

* DISTRIBUTION GRAPH (BY VOL.)



MOPRO CPM-500

PARTICLE ANALYZER

DATE 7/24/68
 SAMPLE SCTD-150
 SOLVENT MT-MED

* CONDITIONS

SOLV. VISC 2.10 CP
 SOLV. DENS 0.794 G/CC
 SHAP. FENS 0.816 G/CC
 D (MM) 16.6 UPT
 D (P) 1.00 UPT
 D (T) 1.00 UPT

SPEED 500. UPT

* TIME 0.0 6.0 12.0 SEC

* DATE

TIME RESPONSE



* DISTRIBUTION TABLE (BY VOL.)

CPM	F12	F122
10.0-6.0	0.0	0.0
10.0-5.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	0.0	0.0
7.00-6.00	0.0	0.0
6.00-5.00	0.0	0.0
5.00-4.00	0.0	0.0
4.00-3.00	12.1	35.0
3.00-2.00	22.4	52.0
2.00-1.00	25.4	75.0
1.00-0.00	7.5	100.0

D (MM) 2.20 UPT

* DISTRIBUTION GRAPH (BY VOL.)



C3 Milling RESULTS - T1: Teflon T2: Polyw T3: Polyl

T1

MODEL: CAPP-502
PARTICLE ANALYZERDATE 5/17
SAMPLE C3-PW
SOLVENT ISO

* CONDITIONS

SOLV. VISC 2.18 cP
SOLV. MEAS 0.7916 cP
SAMP. MEAS 0.5616 cP
D(CORR) 10.0 cP
D(CORR) 1.00 cP
D(CORR) 1.00 cP
SPEED 500. (RPM)

* TIME 0.0 4 MIN 20 SEC

* DATA

TIME RESONANCE



* DISTRIBUTION TABLE (BY VOL.)

D(P2)	F(C2)	D(C2)
10.0-0.0	0.0	0.0
10.0-5.0	3.3	3.2
5.00-0.00	3.6	6.5
0.00-7.00	6.1	13.8
7.00-6.00	7.7	20.7
6.00-5.00	9.5	30.2
5.00-4.00	12.6	42.8
4.00-3.00	15.6	62.4
3.00-2.00	16.0	75.2
2.00-1.00	16.2	95.4
1.00-0.00	4.6	100.0

DOWEL 3.67 cP

* DISTRIBUTION GRAPH (BY VOL.)

MODEL: CAPP-502
PARTICLE ANALYZERDATE 5/17
SAMPLE C3-PW
SOLVENT ISO

* CONDITIONS D=0.9

SOLV. VISC 2.18 cP
SOLV. MEAS 0.7916 cP
SAMP. MEAS 0.5616 cP
D(CORR) 10.0 cP
D(CORR) 1.00 cP
D(CORR) 1.00 cP
SPEED 500. (RPM)

* TIME 0.0 4 MIN 20 SEC

* DATA

TIME RESONANCE

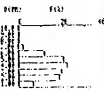


* DISTRIBUTION TABLE (BY VOL.)

D(P2)	F(C2)	D(C2)
10.0-0.0	0.0	0.0
10.0-5.0	0.0	0.0
5.00-0.00	0.0	0.0
0.00-7.00	0.0	0.0
7.00-6.00	2.1	2.1
6.00-5.00	11.5	13.6
5.00-4.00	26.2	33.8
4.00-3.00	21.9	55.7
3.00-2.00	17.4	75.1
2.00-1.00	10.3	93.4
1.00-0.00	6.6	100.0

DOWEL 3.26 cP

* DISTRIBUTION GRAPH (BY VOL.)

MODEL: CAPP-502
PARTICLE ANALYZERDATE 5/17
SAMPLE C3-PW
SOLVENT ISO

* CONDITIONS D=0.9

SOLV. VISC 2.18 cP
SOLV. MEAS 0.7916 cP
SAMP. MEAS 0.5616 cP
D(CORR) 10.0 cP
D(CORR) 1.00 cP
D(CORR) 1.00 cP
SPEED 500. (RPM)

* TIME 0.0 4 MIN 20 SEC

* DATA

TIME RESONANCE



* DISTRIBUTION TABLE (BY VOL.)

D(P2)	F(C2)	D(C2)
10.0-0.0	0.0	0.0
10.0-5.0	0.0	0.0
5.00-0.00	0.0	0.0
0.00-7.00	2.0	21.6
7.00-6.00	6.0	27.7
6.00-5.00	9.2	36.6
5.00-4.00	9.0	46.6
4.00-3.00	12.6	59.2
3.00-2.00	17.6	74.9
2.00-1.00	9.0	86.1
1.00-0.00	9.0	95.6
0.00-0.00	4.2	100.0

DOWEL 4.73 cP

* DISTRIBUTION GRAPH (BY VOL.)



T2 Part I

 HOPPER CPM-501
 PARTICLE ANALYZER

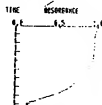
 DATE 5/19
 SAMPLE C3-P2-T2
 SOLVENT 150

• CONDITIONS

 SOLV. VISC. 2.10-10
 SOLV. BESS. 0.750-100
 SHAP. BESS. 6.3616-100
 DENSITY 10.0 1000
 DENSITY 1.00100
 DENSITY 1.00100
 SPEED SAG. 1000

• TIME 0.0 4 MIN 20 SEC

• DATA ~0.9



• DISTRIBUTION TABLE (BY VOL.)

DEPT	F12	F10
10.0-5.0	0.0	0.0
10.0-5.0	5.0	5.0
5.00-0.00	1.4	12.0
0.00-7.00	1.5	14.0
7.00-0.00	4.5	15.0
0.00-5.00	11.2	20.0
5.00-0.00	14.2	44.0
0.00-3.00	15.0	60.0
3.00-0.00	15.0	25.0
2.00-1.00	16.0	27.0
1.00-0.00	2.5	100.0

DENSITY 3.65 1000

• DISTRIBUTION GRAPH (BY VOL.)


 HOPPER CPM-501
 PARTICLE ANALYZER

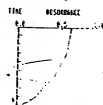
 DATE 5/19
 SAMPLE C3-P2-T2
 SOLVENT 150

• CONDITIONS

 SOLV. VISC. 2.10-10
 SOLV. BESS. 0.750-100
 SHAP. BESS. 6.3616-100
 DENSITY 10.0 1000
 DENSITY 1.00100
 DENSITY 1.00100
 SPEED SAG. 1000

• TIME 0.0 4 MIN 20 SEC

• DATA ~0.57

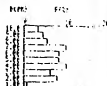


• DISTRIBUTION TABLE (BY VOL.)

DEPT	F12	F10
10.0-5.0	36.0	20.0
10.0-5.0	3.2	30.0
5.00-0.00	4.0	40.0
0.00-7.00	5.0	40.0
7.00-0.00	5.0	50.0
0.00-5.00	12.0	67.0
5.00-0.00	16.0	70.0
0.00-3.00	15.0	45.0
3.00-0.00	4.0	70.0
2.00-1.00	7.0	50.0
1.00-0.00	0.7	100.0

DENSITY 6.36 1000

• DISTRIBUTION GRAPH (BY VOL.)


 HOPPER CPM-501
 PARTICLE ANALYZER

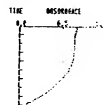
 DATE 5/19
 SAMPLE C3-P2-T2
 SOLVENT 150

• CONDITIONS

 SOLV. VISC. 2.10-10
 SOLV. BESS. 0.750-100
 SHAP. BESS. 6.3616-100
 DENSITY 10.0 1000
 DENSITY 1.00100
 DENSITY 1.00100
 SPEED SAG. 1000

• TIME 0.0 4 MIN 20 SEC

• DATA ~6.7



• DISTRIBUTION TABLE (BY VOL.)

DEPT	F12	F10
10.0-5.0	20.0	20.0
10.0-5.0	2.5	20.0
5.00-0.00	4.0	33.0
0.00-7.00	1.5	33.0
7.00-0.00	4.0	35.0
0.00-5.00	7.5	47.0
5.00-0.00	15.0	61.0
0.00-3.00	12.0	73.0
3.00-0.00	12.0	80.0
2.00-1.00	12.0	90.0
1.00-0.00	1.2	100.0

DENSITY 6.36 1000

• DISTRIBUTION GRAPH (BY VOL.)



Administrative Notes

12 PART 2

MODEL CAP-500
PARTICLE ANALYZER

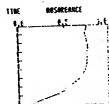
DATE 5/19
SAMPLE R19-12
SOLVENT 150

• CONDITIONS

SOLV. VISC 2.10(CP)
SOLV. DENS 0.7916(G/CC)
SAMP. DENS 0.7616(G/CC)
DCHM2 10.0 (CM)
DCHM3 1.00(CP)
DCHM4 1.00(CP)
DCHM5 1.00(CP)
SPEED 500. (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE ~07

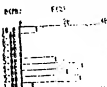


• DISTRIBUTION TABLE (BY VOL.)

CHM2	FCH2	FCH3
10.0-0.0	0.0	0.0
10.0-0.0	7.2	7.2
9.00-8.00	0.0	7.2
8.00-7.00	0.0	7.2
7.00-6.00	0.0	2.2
6.00-5.00	0.3	7.6
5.00-4.00	15.1	22.7
4.00-3.00	22.0	45.7
3.00-2.00	20.0	65.7
2.00-1.00	25.0	90.7
1.00-0.00	4.7	100.0

CHM2 2.50 (CP)

• DISTRIBUTION GRAPH (BY VOL.)



MODEL CAP-500
PARTICLE ANALYZER

DATE 5/19
SAMPLE C3-12
SOLVENT 150

• CONDITIONS

SOLV. VISC 2.10(CP)
SOLV. DENS 0.7916(G/CC)
SAMP. DENS 0.7616(G/CC)
DCHM2 10.0 (CM)
DCHM3 1.00(CP)
DCHM4 1.00(CP)
DCHM5 1.00(CP)
SPEED 500. (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE ~07



• DISTRIBUTION TABLE (BY VOL.)

CHM2	FCH2	FCH3
10.0-0.0	0.0	0.0
10.0-0.0	2.2	2.2
9.00-8.00	3.0	6.0
8.00-7.00	2.7	5.0
7.00-6.00	4.2	16.0
6.00-5.00	10.1	26.0
5.00-4.00	15.0	41.0
4.00-3.00	15.0	60.0
3.00-2.00	21.0	81.0
2.00-1.00	16.0	97.0
1.00-0.00	2.7	100.0

CHM2 2.50 (CP)

• DISTRIBUTION GRAPH (BY VOL.)



MODEL CAP-500
PARTICLE ANALYZER

DATE 5/19/82
SAMPLE C3-12
SOLVENT 150

• CONDITIONS

SOLV. VISC 2.10(CP)
SOLV. DENS 0.7916(G/CC)
SAMP. DENS 0.7616(G/CC)
DCHM2 10.0 (CM)
DCHM3 1.00(CP)
DCHM4 1.00(CP)
DCHM5 1.00(CP)
SPEED 500. (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE

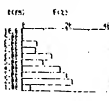


• DISTRIBUTION TABLE (BY VOL.)

CHM2	FCH2	FCH3
10.0-0.0	0.0	0.0
10.0-0.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	7.0	7.0
7.00-6.00	6.0	13.0
6.00-5.00	12.0	26.0
5.00-4.00	5.0	31.0
4.00-3.00	17.1	53.0
3.00-2.00	20.0	73.0
2.00-1.00	22.0	94.0
1.00-0.00	4.0	100.0

CHM2 3.20 (CP)

• DISTRIBUTION GRAPH (BY VOL.)



T2 (cont.)

ANALYSIS: CPM-500
PARTICLE ANALYZER

DATE: 6/19
SAMPLE: CS-25-T2
SOLVENT: 100

* CONDITIONS

SOLV. VISC: 2.10 cP
SOLV. MEAS: 0.7516 cP
SAMP. MEAS: 0.5614 cP
DENS: 10.0 LBS
DENS: 1.00 LBS
DENS: 1.00 LBS
SPEED: 500. CPM

* TIME: 0 H 4 MIN 20 SEC

DATE: 0.87
TIME: 0.87


* DISTRIBUTION TABLE (BY VOL.)

WPM	F(%)	S(%)
10.0-5.0	0.0	0.0
10.0-5.0	1.2	1.2
9.00-8.00	2.8	5.9
8.00-7.00	8.1	6.6
7.00-6.00	4.4	6.4
6.00-5.00	7.3	15.8
5.00-4.00	11.8	27.5
4.00-3.00	26.1	53.7
3.00-2.00	21.2	81.4
2.00-1.00	16.5	91.6
1.00-0.00	3.4	100.0

DENS: 3.24 cP

* DISTRIBUTION GRAPH (BY VOL.)


ANALYSIS: CPM-500
PARTICLE ANALYZER

DATE: 6/19
SAMPLE: CS-25-T2
SOLVENT: 100

* CONDITIONS

SOLV. VISC: 2.10 cP
SOLV. MEAS: 0.7516 cP
SAMP. MEAS: 0.5614 cP
DENS: 10.0 LBS
DENS: 1.00 LBS
DENS: 1.00 LBS
SPEED: 500. CPM

* TIME: 0 H 4 MIN 20 SEC

DATE: 0.9

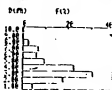


* DISTRIBUTION TABLE (BY VOL.)

WPM	F(%)	S(%)
10.0-5.0	0.0	0.0
10.0-5.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	2.2	2.2
7.00-6.00	0.0	9.1
6.00-5.00	6.0	15.8
5.00-4.00	9.6	26.4
4.00-3.00	22.5	47.7
3.00-2.00	26.1	77.4
2.00-1.00	16.6	95.0
1.00-0.00	3.4	100.0

DENS: 2.91 cP

* DISTRIBUTION GRAPH (BY VOL.)



Administrative Notes

T1 versus T2 versus T3 for various passes

MODEL: CAPP-564
PARTICLE ANALYZER

DATE: 1/11
SAMPLE: C3-P5-B
SOLVENT: 150

• CONDITION: T3
SOLV. VISC: 2.10E-1
SOLV. DENS: 0.7914-CE
SAMP. DENS: 6.3616-CE
DURIN: 10.6 CPT
DURIN: 1.00EPT
DURIN: 1.00EPT
SPEED: SPT. CPT:

• TIME: 0.0 4 MIN 20 SEC

• DATA: 0.9

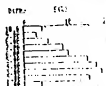
TIME RESONANCE



• DISTRIBUTION TABLE (PT VOL.)

DELTA	F12	F13
10.0 - 0.0	0.0	0.0
10.0 - 5.0	6.2	6.2
9.00-8.00	2.5	7.2
8.00-7.00	5.0	12.7
7.00-6.00	3.8	21.5
6.00-5.00	19.2	21.5
5.00-4.00	16.4	41.9
4.00-3.00	16.4	63.7
3.00-2.00	17.5	61.0
2.00-1.00	15.8	96.8
1.00-0.00	4.8	100.0
DURIN: 3.75 CPT		

• DISTRIBUTION GRAPH (PT VOL.)



MODEL: CAPP-564
PARTICLE ANALYZER

DATE: 1/11
SAMPLE: C3-P5-B
SOLVENT: 150

• CONDITION: T1
SOLV. VISC: 2.10E-1
SOLV. DENS: 0.7914-CE
SAMP. DENS: 6.3616-CE
DURIN: 10.6 CPT
DURIN: 1.00EPT
DURIN: 1.00EPT
SPEED: SPT. CPT:

• TIME: 0.0 4 MIN 20 SEC

• DATA: T1

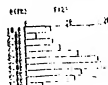
TIME RESONANCE



• DISTRIBUTION TABLE (PT VOL.)

DELTA	F12	F13
10.0 - 0.0	0.0	0.0
10.0 - 5.0	0.0	0.0
9.00-8.00	3.7	0.0
8.00-7.00	0.0	15.4
7.00-6.00	6.2	23.4
6.00-5.00	12.0	25.4
5.00-4.00	16.0	52.0
4.00-3.00	17.0	72.0
3.00-2.00	12.0	85.0
2.00-1.00	11.5	96.0
1.00-0.00	3.7	100.0
DURIN: 4.14 CPT		

• DISTRIBUTION GRAPH (PT VOL.)



MODEL: CAPP-564
PARTICLE ANALYZER

DATE: 1/11
SAMPLE: C3-P5-B
SOLVENT: 150

• CONDITION: T2
SOLV. VISC: 2.10E-1
SOLV. DENS: 0.7914-CE
SAMP. DENS: 6.3616-CE
DURIN: 10.6 CPT
DURIN: 1.00EPT
DURIN: 1.00EPT
SPEED: SPT. CPT:

• TIME: 0.0 4 MIN 20 SEC

• DATA: T2

TIME RESONANCE



• DISTRIBUTION TABLE (PT VOL.)

DELTA	F12	F13
10.0 - 0.0	0.0	0.0
10.0 - 5.0	0.0	6.2
9.00-8.00	4.7	23.2
8.00-7.00	5.0	16.0
7.00-6.00	6.3	23.1
6.00-5.00	16.7	33.7
5.00-4.00	12.7	46.4
4.00-3.00	16.0	63.4
3.00-2.00	10.0	87.4
2.00-1.00	14.7	94.1
1.00-0.00	2.5	100.0
DURIN: 3.75 CPT		

• DISTRIBUTION GRAPH (PT VOL.)



W0156 CAPA-500
PARTICLE 04R, Y214

DATE 5/15/86
SAMPLE C3-P2-T3
SOLVENT ISO

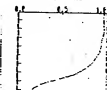
- **COMPILERS**

SOLV.VISC	2.10E-01
SOLV.DENS	0.796E+01
SAMP.DENS	6.34E+00
BCONE	10.0 C/P
BCOIL	1.00E+01
BCOIL2	1.00E+01
SPEED	540. C/P

* TIME 0 r 4 R10 26 SEC

- **MI**

TIME	OBSERVATIONS
0800	Clouds 100% Temp 60° Wind 10 mph Pressure 30.0
0900	Clouds 100% Temp 62° Wind 12 mph Pressure 30.0
1000	Clouds 100% Temp 64° Wind 14 mph Pressure 30.0
1100	Clouds 100% Temp 66° Wind 16 mph Pressure 30.0
1200	Clouds 100% Temp 68° Wind 18 mph Pressure 30.0
1300	Clouds 100% Temp 70° Wind 20 mph Pressure 30.0
1400	Clouds 100% Temp 72° Wind 22 mph Pressure 30.0
1500	Clouds 100% Temp 74° Wind 24 mph Pressure 30.0
1600	Clouds 100% Temp 76° Wind 26 mph Pressure 30.0
1700	Clouds 100% Temp 78° Wind 28 mph Pressure 30.0
1800	Clouds 100% Temp 80° Wind 30 mph Pressure 30.0
1900	Clouds 100% Temp 82° Wind 32 mph Pressure 30.0
2000	Clouds 100% Temp 84° Wind 34 mph Pressure 30.0
2100	Clouds 100% Temp 86° Wind 36 mph Pressure 30.0
2200	Clouds 100% Temp 88° Wind 38 mph Pressure 30.0
2300	Clouds 100% Temp 90° Wind 40 mph Pressure 30.0
2400	Clouds 100% Temp 92° Wind 42 mph Pressure 30.0
2500	Clouds 100% Temp 94° Wind 44 mph Pressure 30.0
2600	Clouds 100% Temp 96° Wind 46 mph Pressure 30.0
2700	Clouds 100% Temp 98° Wind 48 mph Pressure 30.0
2800	Clouds 100% Temp 100° Wind 50 mph Pressure 30.0
2900	Clouds 100% Temp 102° Wind 52 mph Pressure 30.0
3000	Clouds 100% Temp 104° Wind 54 mph Pressure 30.0
3100	Clouds 100% Temp 106° Wind 56 mph Pressure 30.0
3200	Clouds 100% Temp 108° Wind 58 mph Pressure 30.0
3300	Clouds 100% Temp 110° Wind 60 mph Pressure 30.0
3400	Clouds 100% Temp 112° Wind 62 mph Pressure 30.0
3500	Clouds 100% Temp 114° Wind 64 mph Pressure 30.0
3600	Clouds 100% Temp 116° Wind 66 mph Pressure 30.0
3700	Clouds 100% Temp 118° Wind 68 mph Pressure 30.0
3800	Clouds 100% Temp 120° Wind 70 mph Pressure 30.0
3900	Clouds 100% Temp 122° Wind 72 mph Pressure 30.0
4000	Clouds 100% Temp 124° Wind 74 mph Pressure 30.0
4100	Clouds 100% Temp 126° Wind 76 mph Pressure 30.0
4200	Clouds 100% Temp 128° Wind 78 mph Pressure 30.0
4300	Clouds 100% Temp 130° Wind 80 mph Pressure 30.0
4400	Clouds 100% Temp 132° Wind 82 mph Pressure 30.0
4500	Clouds 100% Temp 134° Wind 84 mph Pressure 30.0
4600	Clouds 100% Temp 136° Wind 86 mph Pressure 30.0
4700	Clouds 100% Temp 138° Wind 88 mph Pressure 30.0
4800	Clouds 100% Temp 140° Wind 90 mph Pressure 30.0
4900	Clouds 100% Temp 142° Wind 92 mph Pressure 30.0
5000	Clouds 100% Temp 144° Wind 94 mph Pressure 30.0
5100	Clouds 100% Temp 146° Wind 96 mph Pressure 30.0
5200	Clouds 100% Temp 148° Wind 98 mph Pressure 30.0
5300	Clouds 100% Temp 150° Wind 100 mph Pressure 30.0
5400	Clouds 100% Temp 152° Wind 102 mph Pressure 30.0
5500	Clouds 100% Temp 154° Wind 104 mph Pressure 30.0
5600	Clouds 100% Temp 156° Wind 106 mph Pressure 30.0
5700	Clouds 100% Temp 158° Wind 108 mph Pressure 30.0
5800	Clouds 100% Temp 160° Wind 110 mph Pressure 30.0
5900	Clouds 100% Temp 162° Wind 112 mph Pressure 30.0
6000	Clouds 100% Temp 164° Wind 114 mph Pressure 30.0
6100	Clouds 100% Temp 166° Wind 116 mph Pressure 30.0
6200	Clouds 100% Temp 168° Wind 118 mph Pressure 30.0
6300	Clouds 100% Temp 170° Wind 120 mph Pressure 30.0
6400	Clouds 100% Temp 172° Wind 122 mph Pressure 30.0
6500	Clouds 100% Temp 174° Wind 124 mph Pressure 30.0
6600	Clouds 100% Temp 176° Wind 126 mph Pressure 30.0
6700	Clouds 100% Temp 178° Wind 128 mph Pressure 30.0
6800	Clouds 100% Temp 180° Wind 130 mph Pressure 30.0
6900	Clouds 100% Temp 182° Wind 132 mph Pressure 30.0
7000	Clouds 100% Temp 184° Wind 134 mph Pressure 30.0
7100	Clouds 100% Temp 186° Wind 136 mph Pressure 30.0
7200	Clouds 100% Temp 188° Wind 138 mph Pressure 30.0
7300	Clouds 100% Temp 190° Wind 140 mph Pressure 30.0
7400	Clouds 100% Temp 192° Wind 142 mph Pressure 30.0
7500	Clouds 100% Temp 194° Wind 144 mph Pressure 30.0
7600	Clouds 100% Temp 196° Wind 146 mph Pressure 30.0
7700	Clouds 100% Temp 198° Wind 148 mph Pressure 30.0
7800	Clouds 100% Temp 200° Wind 150 mph Pressure 30.0
7900	Clouds 100% Temp 202° Wind 152 mph Pressure 30.0
8000	Clouds 100% Temp 204° Wind 154 mph Pressure 30.0
8100	Clouds 100% Temp 206°



* DISTRIBUTION TABLE (SEE VOL. 3)

D(%)	F(%)	G(%)
16.6	8.6	6.6
11.4-9.6	1.6	1.6
9.00-8.00	6.6	1.6
8.00-7.00	2.1	4.9
7.00-6.00	4.3	5.2
6.00-5.00	5.4	16.6
5.00-4.00	12.6	31.5
4.00-3.00	26.7	57.2
3.00-2.00	36.8	82.2
2.00-1.00	19.3	96.5
1.00-0.00	3.5	100.0

1. (NAME) 3.11 (pts)

* DISTRIBUTION FROM CPT 251 *



100179

Technical Notebook

Book V

Serials and Last Name:

NCOMBE, P.

Serial:

139

Date of First Entry:

6/7/88

Date of Last Entry:

5/89

Security Classification:

42 11-7-88

IBM Technical Notebook

Survey 2212 starting time versus rel density
rel D(%) wt

✓ 0	68.4	
✓ (0.08)	65.9	69.7
✓ 0.25	61.1	
✓ 0.5	59.7	
(16) (70)	54	↙
✓ 120	51	↙

small pellet, density determination
 probably not as accurate

16h (not listed w book)

POST

0.88 1.15 0.216 0.22 4.0 / 4.45 62

↖
REDO

10-2-88 00011 Analytical IBM Technical Notebook

El.	wt %	theo. M%	Anal M%
Ca	22.4	0.86	0.875
Si	8.24	0.14	0.147
Cu	40.6	1	1

Example calc. ^{Sample normally 48}
 $\frac{Ca\ wt\ \%}{Cu\ wt\ \%} = 0.639 / 1.639 = 1$
 $\frac{Si\ wt\ \%}{Cu\ wt\ \%} = 0.094 / 1.639 = 0.147$
 $\frac{Cu\ wt\ \%}{Cu\ wt\ \%} = 0.539 = 0.875$

11/3 0011 pellet 2 for 16h diffusion sinter
 Pre 4000/30,000 slightly irregular

2.85	1.531	0.496	0.913	~3.12	/4.95 = 63 — perfect
2.81	~1.36	0.44	0.625	4.4	↓ = <u>89</u>
			0.64		

0201 4000/30,000 PG

3.78	1.365	0.494	0.723	5.23	= 72.4% (too high?)
------	-------	-------	-------	------	---------------------

11/4 0011-2 cut into 2 slices. Didn't add block thickness so irregular.
 1 ~ 2.30 cm thick 1 ~ 0.179 cm

Post will use for first press
 875C for 30 hrs → pellet has warped, grown large nodule like
 xstals and sagged. Obviously metastable.
 previous 3h sinter showed no evidence of instability.

11-2-88

IBM Technical Notebook

44 11-9 2201 pellets
 3200/28
 2013 2.99 1.351 0.415 0.595 5.02 69.7
 2.96 ~1.306 0.392 0.498 ~5.98 ~83.3+
 2-3 min 872C SINTER (SLD ATTAINMENT 12 min TENSUS 1. $T_{tot} = T_{AT} + 3 \text{ min}$)
 3300/30
 2014 1.16 1.082 0.245 0.225 5.16 71.7
 1.15 1.050 2.10 0.182 6.32 87.5
 2015 1.17 1.086 0.248 0.230 5.09 70.7
 Reground Repressed } pellet 201-112
 2016 0.97 1.094 0.205 0.193 5.13 71.25
 * 0.98 1.06 0.185^{up} 0.163 6.01 83.5
 * 0.178 0.158 6.2 86
 to temp 1845
 out 2.15
 30 min
 * (f): 20-45 some evidence of drooping
 edge droop in pellet. reduce temp 5C
 2700/29
 2017 1.2 1.086 0.258 0.238(5) 5.03 69.9
 1.01 1.06 1.19 1.05 ~0.225 0.195 6.1 84.7
 to temp 2227-8
 15
 15

The above understood

Date

and

Date

11-10 ENTERING SUMMARY IBM Technical Notebook <2201 data>

	temp	SWITCH	green	POST	201-2
201-8	872C	2min	71.25	85.6 ←	011-2201 P3 pressed pallet
201-3	872	12-3	69.7	86	
201-4	875C	5	71.7	87.5	(larger die)
201-9	872C	5	71-	84.7	8%. lane
201-7	872C	15	69.9	84.7	
201-6	875C	30	71.25	88.5	
201-10	872C	1h	70.4	86.3	85
201-1	875 ^{POF}	2h		84-	
201-2	875	30h		(76.1) = 79	

W. L. ...
...

Record keeping: $\begin{cases} 201-2 & 30h \text{ } 875^{\circ}C \sim 75\% \text{ (yr)}: \text{irregular pellet growth} \\ & \text{resulting in varying local densities} \\ 201-3 & 0.608 \text{ dia. pellet for pressure distribution} \\ 201-5 & \text{reg'd} \rightarrow 201-11 \end{cases}$

11-H Gas pycnometry gives an averaged vol density for pellets 1, 3, 9 (weight 4.6g) of 86.75g vs 84.75 (reasonable agreement), mostly closed porosity.

46-14 SINTER 870-875C IBM Technical Notebook

NOTE: [ALL SINTER TIMES ARE 1 MW attainment + 1 MW EQ SOAK + Δ SINTER time]

201-8 refect pellet ~3000/29000

POST	1.19	1.081	0.253	0.232	5.13	71.25	green
2 MW	1.17	1.038	0.225	0.190	6.16	85.6	

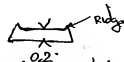
POST	201-9 12	1.075	0.259	0.235	5.11	71.00	green
5 MW	1.019	1.036	0.231	0.195	6.10	84.7	

POST	201-10 1.10	1.083	0.236	0.217	5.07	70.4	
1h	1.09	1.057*	0.21*	0.175(5)	6.21	85.25 (accurate?)	

201-11 Pellet was regd & regressed from broken pellet. Also, die ran from resulting in much higher uniaxial pressure (if true edge) 12,000

1.169	0.252	0.240	5.04	70.06
-------	-------	-------	------	-------

* linear average dia due to slumping (-) w pellet interior after edge ridge worn away



? probably slightly less due to exclusion of ridge volume and linear approx. after flattening; 15 μ m

201-10 0.90* 1.057 0.168 0.147 6.12 85 better (more accurate)

11 2.96 (218) 201-11 1.357 0.412 0.596 4. 5.0 (69.4)

2.935 1.315 0.365 0.496 5.94 82.5

11-12

201-11 cut what larger flattened and polished.

0011-2201 sandwich ~0.353-0.363 thick.

> From surface top to bottom of "weight plate" $1\frac{1}{32}$ " @ 462C
assuming ~6 lbs force ram { plate { x-sectional pellet area
of 0.212 in^2 load \Rightarrow 2.8 psi

Diffusion starting at @ 860C for ~12 hrs.

Rel density from measurement of 201-11 ~83%. On inspection of internal polished surface numerous buevoid-like occlusions present. Some degree of open porosity, also.

Pyc. rel. den = 88. % thus Δ attributable to open porosity.

0011 rel density from measure ~89%. No pyc reading done. 16 hr @ 975C.

4:30 pm. T @ 859C assume start of diffusion starting

Plate height $1\frac{1}{8}$ " ($\frac{3}{32}$ " expansion due to TCE from 462C)
No RT measure made, but not significant

48

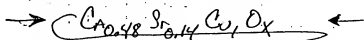
IBM Technical Notebook

11-28-88 <INSERT>

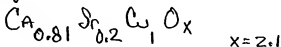
Results (by microprobe) of CaSrCuO_x melt xstals

Melt composition was from pgs. 27-29

Composition was not $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_1\text{O}_x$ in melt, but rather



from which xstals grew of CaSrCuO_x with stois.



Atomic weight fractions were:

Ca	0.195
Sr	0.05
Cu	0.242
O	0.513 (by difference)

Melt temp. was 1000C for 16h with cooling naturally, but
NOT TOTALLY A QUENCH. UNCONTROLLED RATE REGULATED BY PLEASURE
therminal mass

11-22

Balance Bi Powder for Run

2212 - ^{~g} 30.5

2201 - 12.5

0011 - 33.5

2nd Diffusion Run 2hr ramp to 866C @ 100C plate space = 1 7/32

0011 disc started @ 0.18 cm (not measured above Si disk, rather was (2201 or standard, will try to appox))

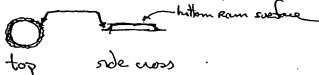
2201 ~ same 0.18

loose ~ 0.23 - 0.2 x 0.03/sketch ∴ 0.18 → 0.15, 0.17 → 0.14
 so standard might be ~ 0.29 cm (80% of Run #1)

Approx thickness by height of plate differences @ 866C 1 7/32 - 1 3/32

7/32 - 0.23 cm ∴ 0.29 - 0.23 = 0.06 too small → 871C peak

RESULTS: "Bi" pellet has spread, apparently melting. Total thickness 0.18 cm
 has generated crystalline (S) skirt around pellet periphery.



0.18 cm = 0.07" slice ~ square 0.07 + 0.015 = 0.085

50

IBM Technical Notebook

0011-2201 Mix Calculations

wt% wt%
90.11 2201.

 $+2$

~~1~~✓ +5

$$\text{B}_2\text{S}_2\text{C}_4\text{C}_2\text{O}_8$$
$$B_{L2} S_{R2} C_{A0} \omega_1 \theta_b$$
$$B^3, S^2, C^1, O^1, O_2$$

From "ideal" store.

$$\begin{array}{ccc} 2201 & + & 0011 \rightarrow 2212 \\ 1 \text{ mole} & & 1 \text{ mole} \end{array}$$

	A.W.	0011	Inde	Inde	Inde
B _c	208.98	-	22.01	477.96	221.2
S _c	27.62	-	175.24	477.96	175.24
C _A	40.08	40.08	-	40.08	40.08
C _w	63.54	63.54	63.54	127.08	127.08
D	15.9974		95.9964	127.9952	

$$135.6188 + 752.7341 = 888.3529$$

B _L	0.44(1.19)	2.45(1.16)(0.1)	2.35(1.16)(1.19)(2)
	—	449.307	449.307
Sn	12.2468	140.192	147.2016
Ca	34.488	—	40.3284%
Cu	63.54	63.54	127.08
O	31.9988	95.9964*	127.9952

142.2744 749.0354 $891.912296 / (891.3098)$
 $\% \text{ dev}$ $+ 8.6\%$ \uparrow

+8.6%

$$\begin{array}{r} *(5.825)15.9994 \\ 93.19651 \end{array}$$

99.6% (~~etc~~ / 2.15 etc)

The above understood
and witnessed by

Date _____ and _____

Date: _____

IBM Technical Notebook

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CONTINUATION...

$$1 \text{ mole } ^{22}\text{O}^{11} + 1 \text{ mole } ^{22}\text{O}^{11} \rightarrow \text{O}^{11} + 529 \text{ wt } \% ^{22}\text{O}^{11}$$

142.2744g 752.7364g

$$142.2744g + (0.02)(142.2744g) = 145.12g$$

2.84549g

9.49g 0.19g

9.485g 9.675g

2 wt % batch size

$$142.2744g + (0.05)(142.2744g) = 149.38812g$$

7.11372g

9.485g 0.475g

0.48g 9.96g

5 wt % batch size

For Stoic (molar) mix = $1.423g + 7.53g = 8.95g$ batch size

Total Usage	0011	2201	8g
	20.393	8.192	8
%	61	66	

	cc	cc	vol %	wt %
roll	2.37	0.0264	1.0%	2
table	2.37	0.0736	3	5
	0.356	1.045	25%	stic

Stoic:	2201	8g	5r	Ca	C
	2.15	1.6	0	1	

0011	0	0.14	0.86	1	
	2.15	1.74	0.86	2	versus poly 2.15 1.68 1.12 2

The above understood
and witnessed by

Date

and
by

Date

52 Stoic MIXING

IBM Technical Notebook

0011 2201

~1.43 g ~7.53

MX STARTING @ 3:00 P.M., 50mls isopropyl
5cc ZrO_2 balls
2/3 full

NOTE: From bottom pg 51 can be seen this additive approach will
yield a theoretical molar comp { 0.1 M larger in Sr
0.31 M less in Ca

i.e. Strontia rich, Calcium poor

8.96 g added initially, 8.85 g recovered: 1.2% loss (98.8 yield)

Stoic 1 Pre 2700/27,500

3.11 1.36 0.486 0.706 4.41 ~68.9

$0.25(4) + 0.75(7.2) = 6.4$ vol% basis, ~ density calc

Rw. (SINTER) temp to be 852C

Pellet melted indicating lower mp. lig ϕ exists in system of later
xstallized. Predominantly 1 bath-like ϕ w/ exaggerated growth
as in 2201 12oh sample.

12-5

4:20 P.M. // 4:25 @ temp.

0011-3 placed in preheated rapid temp set @ 951C ($T_{\text{temp}} = 975C$)
for overnite sintering.
No. per data on density due to irregular shape caused by
pellet crumbling during isopressing.
unipress \rightarrow 6000, 150-29,000 PSI. wght \sim 3.1g ^{3.0-2.9}

12/6

9:30 Slow cooling begun $\therefore \Delta T_{\text{inter}} = 17h @ 875C$

Post 2.86g \sim 0.460 mm thick. radius might have been \sim 1.80

estimated density 0.666cc @ 3.1g \sim 4.66 / 7.00 \approx 93 (may be high)
3.0 4.5 \downarrow 90 better

0011-3

0.181" thick

Slice 1 \rightarrow 0.09" after cleaning // post polish \rightarrow N/R

Slice 2 \rightarrow 0.074
0.179 ✓

2201-8 1.088 dia \therefore area = $\pi D^2/4 = 0.85 \text{ in}^2$
0.409 \sim 0.525 in^2 5.75 lbs / .525 $\text{in}^2 \sim$ 11 psi

2201-8 (top)



Pellet configuration @ START \sim 3:55 p.m. thickness - 0.34 mm

0011-3

Ramp \rightarrow 434 Set point - 800C Dwell - 12h 1 1/2 @ 380C

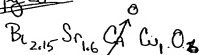
12/7 Result: no melting, pellets bonded by little deformation.

12/8 After 24h 825C anneal no evidence of lic., but bond breaks
after handling at pellet interface with some "rxn etching" of
0011 pellet surface leaving thin ^{upper} layer of 2201 (or rxn prod)
behind.

IBM Technical Notebook

54
12-6

SECOND 2201 Synthesis



$\text{Bi} \rightarrow \text{Bi}_2\text{O}_3 : 30.0543 \times 2 = 60.1086 \quad 60.11$

$\text{Sr} \rightarrow \text{SrCO}_3 : 14.1724 \quad 28.3448 \quad 28.35$

$\text{Cu} \rightarrow \text{CuO} : 4.7724 \quad 9.5448 \rightarrow 9.54$
 $48.9991 \text{ g} \quad 97.9982 \text{ g}$

$\sim 0.7019 \text{ conversion factor for } \text{CO}_2 \rightarrow 0 \quad 28.3448 (0.7019) = 19.898$

Estimate ~ 89 g "batch recovery" $\frac{97.9982}{89.55} \text{ CO}_2 \text{ loss}$

12-7

Bi_2O_3
 $\frac{202.54}{262.68}$
 $60.13 - 60.11 = +0.02 \checkmark$

SrCO_3
 $\frac{291.03}{262.68}$
 $291.03 \leftarrow 27.3835 \text{ wgt } 28.36 \text{ theoretical } 28.36$
 $26.35 \quad \Delta \checkmark$

CuO
 $\frac{300.57}{291.03}$
 $300.57 (9.54) \text{ wgt } 9.55$
 $9.54 \quad \Delta \checkmark$

12-8

97.92 / recovery after drying overnite

$98.02 \text{ theoretical} = 99.9\% \text{ yield } 0.1\% \text{ mixing loss}$

to pg 56

IBM Technical Notebook

55

12-7-88

0.11
9.49
9.48
0.02
9.46

EH

2201

0.48
0.50
0.01
0.49

theor.

weigh

reads

actual = 9.95

std. 1.15h 5min ZnO/IsO
grind mix, screening & drying.

12-8-88

Recovery : 9.84 g / 9.86 g theoretical = 99.8% > 0.2% loss

60.87
cont. take 51.04/5
9.83 trans reads

0011-2201-5W(3V)-1

Post 8500/29,000

2.31 1.17 0.704 0.690 3.35 ~ 67%

Pellet lighter than usual, 1.75g max in future might be considered.

1.183 0.715 CRACKED, measurements ~~1.17~~

12-9

5W-2 900C 8500/39,000

1.27 1.174 0.382 0.414 3.07 61.4!

3:55 w preheated furnace → 4:00 to temp @ 900C

POST 5 MIN

1.24 1.111 0.36 0.349 3.55 71—

15 MIN NO SIGNIFICANT CHANGE

12-12 to temp ~ 10:20 A.M. (check: 10.45 → no slumping) → WATER till 12:30

12:15 A.M.

11.45

~ 2h

1.24 1.055 0.33 0.29 4.28 ~ 86%

The above understood
and witnessed by

Date

and

Date

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IBM Technical Notebook

12-8-88 2201 SynII cont. (from pg 54)

crucible temp $\frac{186.68}{88.79} \rightarrow 186.68 \rightarrow 192.29$ w/ top
 $\frac{186.68}{88.79} = 97.89$

10:00 AM \rightarrow 575C hold 1h
 11:00 \rightarrow 800C
 12-9 11:00 AM cool, required to < 100 mesh

$\frac{182.23}{88.95} = 93.28$ (weight after sintered pack body removed)

$\frac{93.97}{88.95} = 106.78$ if 88.79 used
 $\frac{184.02}{88.95} = 206.88$ after grinding
 $\frac{92.07}{88.95} = 103.51$ to temp. (866C) @ 1:00 p.m.
 $\Delta 1.21$ w grinding 1.3%
 $97.88 - 93.28 = 4.60$
 $97.89 - 89.55 = 8.34$ } 55% REACTED

1:00 - 5:00 PM 866C, shut down for weekend (very resistant sun eye)

12-12-88

to temp 866C @ 10:00 A.M.
 off @ 7:00 A.M. 12/13/88

PARTIAL MELTING, "CLASSIC" EUTECTIC lamellar and large 2201 bathes.

case and sign every entry, have
entry witnessed. Submit an inven-
anything possibly missing and content.

Y possibly important
Disclosure of

☐ Undersified
☐ IBM Internal Use
☐ For External

☐ IBM Confidential-Restricted
☐ Registered IBM Confidential
*Register with local Recorder

12-14-88 2201 Sys III

IBM Technical Notebook

57

Working on bus 202.75

The above understood
and witnessed by _____

Date _____

and
by _____

Date _____

58. 12-14-88 SYN III 2201 IBM Technical Notebook

mixing jar tare 202.75

Be as Be_2O_3 30.0543

Sr as $SrCO_3$ 19.1724

Cu as CuO 4.7724

x 2

= 60.11

28.35

9.55

98.01

- 8.5 CO_2 loss

89.51

$Sr/Be = 0.744$

Sr 0.8 $Sr = 1.72$

Be_2O_3 262.86

tare 202.75

60.11

291.20(19)

262.86

28.34(5)

300.75

291.20

9.55

PRE CAL I

crucible + 185.84

tare 87.99

97.85

97.85/98.01 0.2% max loss

12-20 Post 750C 16h calcination

crucible + 181.15

↓

87.98

93.17

post gen 92.70

no RXN w/ Pt.; lime green color/bottom, uniform throat
except for top 1/2 edges (grey)

93.17 - 97.85 = -4.68 / 8.5 = 55.5% CO_2 lost

post gen

crucible + 180.70

↓

87.98

(92.72)

12-21-88 Post 1700C 20h calcination

178.10

87.98

90.12

Material looks very good, smooth, indicating similar structure
Uniformly black, sparkling, similar body. An outer shell
is 89 ≈ RXN close to completion at 98%
and inner core structure. (see below)



(inner surface core
outer shell
air space)

The above understood
and witnessed by _____

Date

and
by

Date

to page 60

IBM Technical Notebook

12-14-8

$Y_1Ba_2Cu_3O_x$ Implantation Experiment

PRE - film on $SrTiO_3$ 3500/39000

3.07 0.448 0.485 0.799 3.84 ~60.4 %



line 'MARKER' || to long axis of triangular $SrTiO_3$ implant
implant orientation - NOTE: MARK ON UNDERSIDE of pellet

film side opposite

3.02 1.271 0.3% 0.508 6.02 94-95

3.05 1.448 0.476 0.784 3.89 ~61



line 'MARKER' || to long cutting axis of two pellets (cut on line)
implant orientation - see NOTE above for polished side over

2.99 1.272 0.371 0.497 6.02 94-95

3

5:12 p.m. 475C @ 10C/mw to 975 $\Delta 5000/10C/MIN = 50 MIN$ N 6:00 PM

Cutting $SrTiO_3$ implant: measured 0.5" on SAW (0.085-0.505 tangents)

$\frac{1.272}{2.54} = 0.498$ ✓

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and witnessed by

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12-21-88 Cakination III 2201-B3

X-RAY SHOWS DISTINCTLY NOT SINGLE ϕ , even though material looks "ak"

total 177.04
 cur 87.98
 89.06 88.2

12-22-88

175.7 (-1.34) slight sticking (pin) w/ curve bottom
 87.98
 87.92 - 89.51 (theo.) = 1.59 g greater than theoretical loss.
 could be grinding loss 2%

RF
 850 cal

174.93 total
 87.93 tare (after acid cleavage)
 87. - g 0.72 g grinding loss (consistent w/ previous losses)
 + X-ray slide

POST
 12-22-88

174.83
 87.93
 86.90 - 10.10 100% RYAL 1 new strong weight
 not superconcluding but not surprising
 batch #1 wasn't either

IBM Technical Notebook

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12-27-88

Summary various RKN pellets:

5 wt% 2201 in 0011 for 16h @ 850C SEM

5 wt% 2201 in 0011 for 2h @ 975C SEM

{ 0011-2201 ^{5 wt% 2201} ~~microtype~~ ~~pressure treated~~ pellet: 13h 850C } later
lig. formation, exaggerated grain growth/warpage

0011 @ 975C 17h SEM STD.

2201 @ 875C 1h SEM STD.

2212 @ 853C 5min SEM STD.

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and
by

Date

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12-29-80

Dave's Compositions

$\#$	Y	Ba	Cu	Y	Ba	Cu
	(0.157)	(0.33)	(0.50)	0.17	0.33	0.50
	0.15	0.33	0.52	0.0634	1.9838	3—
	0.17	0.35	0.48	1.0625	2.1875	3—
	0.19	0.33	0.48	1.1875	2.0625	3—
	0.19	0.31	0.50	1.14	1.86	3—

Calculated Compositions (calculations next page)

$\#$	Y	Ba*	Cu	total	
1)	1.91937 (1.92)	6.51253 (6.51)	3.97697 (3.98)	12.48	←
2)	1.69356 (1.69)	6.51253 (6.51)	4.13605 (4.14)	12.34	←
3)	1.92	6.90723 (6.91)	3.81789 (3.82)	12.65	
4)	2.14518 (2.15)	6.51 0.33	3.82 0.48	12.48	←
5)	2.15	6.1783 (6.18) 3.1	3.98	12.31	←

* Ba as $BaCO_3$
Y as $\frac{1}{2} O_3$
Cu as CuO } note → no purity corrections applied yet

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by

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1/3/89

Calculations for weights summarized on page 62

2) $Y_{0.15} Ba_{0.33} Co_{0.52}$

$Y = 0.15 (225.8082) / 2 = 16.9356 g Y_2O_3$

$Ba = 0.33 (197.3494) = 65.1253 g BaCO_3$

$Co = 0.52 (79.5394) = 41.3605 g Co$

3) $Y_{0.17} Ba_{0.35} Co_{0.48}$

$Y = 0.17 (225.8082) / 2 = 19.1937 g Y_2O_3$

$Ba = 0.35 () = 69.0783 g BaCO_3$

$Co = 0.48 () = 38.1789 g Co$

4) $Y_{0.19} Ba_{0.33} Co_{0.48}$

$Y = 21.4518 Ba = 65.1253 Co = 38.1789$

5) $Y_{0.19} Ba_{0.31} Co_{0.50}$

$Y = 21.4518 Ba = 61.1783 Co = 39.7697$

1) $Y_{0.17} Ba_{0.33} Co_{0.50}$

$19.1937 65.1253 39.7697$

1/8/89

64

1) ~~88.53~~ (trial #1)
O₂ S₁ 5125

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2 → 88.5409 1.17 Ba₂₃ Cu₅

Y₂O₃ - 1.92

CoO - 3.98(1)

BaCO₃ = 6.51 ~~6.58~~ ^{3.85}

88.53
tare 76.06
12.47

2.3125
0.3900

✓

4.3712
0.3900

6.9665
~~6.5777~~ 6.9685
0.3888

post day 12.43

1.922

3.98(2)

6.5777 = 1248

→ 99.6% recovery total - Δ = 0.05

1-9-89

10.95 g after 2nd 16h 950C O₂ calcination

6.5777 $\left(\frac{153.8391}{197.3510} \right) = 5.11$ - Δ 1.47

12.43

1.47

0.777

13.96

1/17 Dave's post 1h grind = 1.86 μm 3000/30,000

P1 168 1.136 0.968 0.4135 4.06 63.8%

In O₂ @ ~3:00 p.m. 1/19/89, to temp @ 950C projected 4:30 5:00 → 9:00

16h

1.64 1.011 0.354 0.284 5.775 90.8 (91)

1/4/88

4) ~~82~~ fired
O₂

Y_{0.19} Ba_{0.83} Co_{0.98}

~~1.89~~ 6.51 ~~3.14~~
~ 2.15 3.82

3.8217

3.865

4.2082

Y₂O₃ -

~~2.5392~~ ~~6.9623~~ ~~4.2093~~
~~0.3885~~ ~~0.384~~ ~~0.3865~~
2.1477 6.5783 3.8218

⇒ 12.55 g

1/10/88

Second calcination started after grinding. No evidence of
lig formation. Powder looks good already.

10.99 g after 2nd calcination;

10.76 post grind

~~10.76~~ (0.777) = 5.11 - Δ 1.47

12.55
1.47
11.08 g expended: 1099 ✓

Recovered

1/17

P1 Pre 2500/30,000 to temp @ ~ 5:00 pm.

1.60 1.14 0.399 0.4073 3.93 62% ✓

1/18

1.58 1.055 ~ 0.365 0.319 4.95 77.8%

Green peaks coming up in x-ray.

66

IBM Technical Notebook

5) 4.19 Bc 0.31 C 0.50

(99) $\int_0^1 0.5 - 2.14(1/3)$ $2.5760 \rightarrow B(0.5) = 6.17(96)$ $6.0 - 3.9810$ 2

$0.99 \Rightarrow 6.2407$ 4.2092 12.37

2.3761 6.4690 4.2092

0.2287 0.2229 0.2282

2.1474 6.2411 $3.9810 \Rightarrow 12.3695$

12.34(3) collect of the mix // 12.34/12.37 $\sim \Delta 0.24\%$ ✓

$6.2411 - 4.8493 = 1.392$

62.60 62.20

51.17 51.17

12.33 11.03

$- \Delta 1.3 / 1.37 = 93.5\%$

11.00 post grand 62.17 post CII 62.11 11.63

51.18 10.99 10.88

10.95

Post grand 10.46

PRE 1.60 1.440 0.244 0.40 4.00 62.9

Post 1.56 1.266 0.210 0.244 6.00 $(94 \rightarrow 91)$

Good densification, no apparent liq, CII islands present.

The above understood and witnessed by

Date

and by

Date

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2201

P1B3 2500/30000
PRE 1.94 1.09 0.391 0.365 5.315 73.8 %
Post 15 min @ 860
1.94 1.06 0.355 0.313 6.2 86 %

2 wt % 2201 in 0011 1/18/88

9.49
0.19
9.58 some leaking during 0.5 h mix : 9.05 g
9.05 g
8.68 g / Small
0.37 g loss
8.68 g
0.37 g

2 wt % P1 4200/30,000 to temp @ ~5:00 p.m.
PRE 1:70 1.163 0.499 0.53 3.21 ~64.2
1.69 1.21 0.525 0.60 2.82 56.4
1.194-1.227
some slumping
-Δ 12%

Guts yield: 1.57 mm inside -0.30
1.12 mm center 0.25
poked → 1.79 mm outside 0.380 (twice)

+ 26.52 26.03 25.94
post 26.52 25.52 25.45
1.00 → 1000 μm 490

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and witnessed by

Date

and

Date

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2) $\frac{40.15 \text{ BaO} \cdot 0.33 \text{ Cu}_2\text{O}}{42 \text{ O}_3 - 1.6936 \text{ BaO} - 6.5125 \text{ Cu}_2\text{O} - 4.1361}$

(2270.5) $\frac{1.9206}{0.2284(8)} \sim 1.6936$ $\frac{6.8066}{0.2284(8)} - 6.5782$ $\frac{4.3651}{0.2284} - 4.1361$ $\frac{\text{total}}{(2270.5) \sim 12.41}$

1/17 ST CALCINATION $\frac{66.53}{54.16} \frac{(12.37 \text{ measured from weighing})}{12.37} \sim 12.41 = -\Delta 0.3\%$

$6.5183(2.77) = 5.111 (-1.47) \frac{12.37}{-1.47} \sim 10.90$ expected yield (less transfer losses)

1/18 POST $\frac{66.53}{65.15(05)} - \Delta \frac{1.38(48)}{54.20}$ recovery $\frac{65.05}{54.2} \frac{10.85}{10.85}$ total rxn

2nd CAL (16h as above)

1/19 POST $\frac{65.02}{54.2} \frac{10.82}{10.82} \sim \text{constant } 10.79 \text{ recovery}$

Notes: Large liq stains (formation) during 1st/2nd cal unlike

PRE P1 $\frac{1.4}{3300/30000}$ where liq was suppressed in 1st cal { minor in 2nd }
 75C @ 5:16. temp @ 7:45, 16h 11:45 AM 6:40 PM

1.60 1.414 0.258 0.405 3.95 62.1%

1.57 1.227 0.216 0.255 6.16 96.9

The above understood

Date

and

Date

1) ∂_z

4) ∂_2

202

book 3) 1h iso
02

$$PSD \propto \frac{1}{\omega^2}$$

69

NAME: 110-89
 SHEET: 1 OF 2
 DATE: 10-2-85
 TIME: 10:05 AM

* CONTINUING *

SNAKEWISE 2.1417E+07
 SNAKEWISE 6.3547E+06
 BOMBED 1.1417E+07
 BOMBED 1.1417E+07
 BOMBED 1.1417E+07
 BOMBED 1.1417E+07
 BOMBED 1.1417E+07

* TIME: 0.0 4.000 20.000
 * DATA *
 TIME RESPONSE
 0.0 0.000
 4.0 0.000
 20.0 0.000

* DISTRIBUTION TABLE (BY VOL %) *
 BOMBED (1) (2) (3)
 10.0-0 1.0 1.0
 10.0-1 1.0 1.0
 10.0-2 1.0 1.0
 10.0-3 1.0 1.0
 10.0-4 1.0 1.0
 10.0-5 1.0 1.0
 10.0-6 1.0 1.0
 10.0-7 1.0 1.0
 10.0-8 1.0 1.0
 10.0-9 1.0 1.0
 10.0-10 1.0 1.0
 10.0-11 1.0 1.0
 10.0-12 1.0 1.0
 10.0-13 1.0 1.0
 10.0-14 1.0 1.0
 10.0-15 1.0 1.0
 10.0-16 1.0 1.0
 10.0-17 1.0 1.0
 10.0-18 1.0 1.0
 10.0-19 1.0 1.0
 10.0-20 1.0 1.0
 10.0-21 1.0 1.0
 10.0-22 1.0 1.0
 10.0-23 1.0 1.0
 10.0-24 1.0 1.0
 10.0-25 1.0 1.0
 10.0-26 1.0 1.0
 10.0-27 1.0 1.0
 10.0-28 1.0 1.0
 10.0-29 1.0 1.0
 10.0-30 1.0 1.0
 10.0-31 1.0 1.0
 10.0-32 1.0 1.0
 10.0-33 1.0 1.0
 10.0-34 1.0 1.0
 10.0-35 1.0 1.0
 10.0-36 1.0 1.0
 10.0-37 1.0 1.0
 10.0-38 1.0 1.0
 10.0-39 1.0 1.0
 10.0-40 1.0 1.0
 10.0-41 1.0 1.0
 10.0-42 1.0 1.0
 10.0-43 1.0 1.0
 10.0-44 1.0 1.0
 10.0-45 1.0 1.0
 10.0-46 1.0 1.0
 10.0-47 1.0 1.0
 10.0-48 1.0 1.0
 10.0-49 1.0 1.0
 10.0-50 1.0 1.0
 10.0-51 1.0 1.0
 10.0-52 1.0 1.0
 10.0-53 1.0 1.0
 10.0-54 1.0 1.0
 10.0-55 1.0 1.0
 10.0-56 1.0 1.0
 10.0-57 1.0 1.0
 10.0-58 1.0 1.0
 10.0-59 1.0 1.0
 10.0-60 1.0 1.0
 10.0-61 1.0 1.0
 10.0-62 1.0 1.0
 10.0-63 1.0 1.0
 10.0-64 1.0 1.0
 10.0-65 1.0 1.0
 10.0-66 1.0 1.0
 10.0-67 1.0 1.0
 10.0-68 1.0 1.0
 10.0-69 1.0 1.0
 10.0-70 1.0 1.0
 10.0-71 1.0 1.0
 10.0-72 1.0 1.0
 10.0-73 1.0 1.0
 10.0-74 1.0 1.0
 10.0-75 1.0 1.0
 10.0-76 1.0 1.0
 10.0-77 1.0 1.0
 10.0-78 1.0 1.0
 10.0-79 1.0 1.0
 10.0-80 1.0 1.0
 10.0-81 1.0 1.0
 10.0-82 1.0 1.0
 10.0-83 1.0 1.0
 10.0-84 1.0 1.0
 10.0-85 1.0 1.0
 10.0-86 1.0 1.0
 10.0-87 1.0 1.0
 10.0-88 1.0 1.0
 10.0-89 1.0 1.0
 10.0-90 1.0 1.0
 10.0-91 1.0 1.0
 10.0-92 1.0 1.0
 10.0-93 1.0 1.0
 10.0-94 1.0 1.0
 10.0-95 1.0 1.0
 10.0-96 1.0 1.0
 10.0-97 1.0 1.0
 10.0-98 1.0 1.0
 10.0-99 1.0 1.0
 10.0-100 1.0 1.0

* DISTRIBUTION GRAPH (BY VOL %) *
 BOMBED (1) (2)

VOL %
 0 10 20 30 40 50 60 70 80 90 100
 0 10 20 30 40 50 60 70 80 90 100

[illegible][illegible][illegible][illegible]

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and witnessed by _____

Date _____

and

Date _____

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$S_{r, C_{12}O} \rightarrow S_{0.37 C_{0.63} O_{19}}$

$S_{r, O}$	$C_{12}O$
38.34	50.1078

$$\text{SeLDO} \rightarrow \text{Se}_{0.5}\text{L}_{0.5}\text{DO} \quad 51.8037 \quad 39.7697$$

$$S_{C2} \text{ C.O.} \rightarrow S_{C67} \text{ C.O.} \rightarrow 69.4250 \text{ Zr. 248}$$

$$\text{SrO} = 103.6194 \rightarrow \text{SrCO}_3 = 147.63 \quad | 4247$$

$$C_0 = 79.5394$$

3.83. 6.02

3.834 5.0198 \rightarrow 8.8538

(5.18097 - 3.9297) \rightarrow 9.1579

$(6.9425 - 26.248) \cdot 263 \rightarrow 9.5673$

—V—

✓

546 5.02 10.48

7.38 . . 3.98 . . 11.36

9.89 26.34 12.52

540.

CC

IBM Technical Notebook

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1/17/89

CO11-5 c1% 203 @ 850C for attempted TCR prep.

slice 2 - 1.28 mm - 1280 μ m

slice 3 - 0.68 680 μ m

slice 2 prep: mounted side 1 measures 27.64

$$\begin{array}{r} \text{sum: } 300 \mu \\ 12.80 \\ \hline 980/2 = 490 - 490 \\ \hline 850 \text{ target} \end{array} \quad \begin{array}{r} 26.30 - (33) \\ \hline 1.34 - 1.29 \end{array}$$

20 8's on "soft" 15 μ m grids \sim 900 { 150 8's on 6 give 770
720 μ m before starting second side

$$\begin{array}{r} 26.40 \text{ after mount } 30 \rightarrow 26.21 \\ 25.69 \\ \hline 0.71 \checkmark \end{array} \quad \begin{array}{r} 25.69 \\ \hline 520 \end{array}$$

$$\begin{array}{r} 150 \rightarrow 26.16 \\ \hline 14130 \end{array}$$

$$\begin{array}{r} 150 \text{ } 6 \frac{1}{2} \rightarrow 26.06 \\ \hline 390 \checkmark \end{array}$$

The above understood
and witnessed by

Date

and

Date

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3) O_2 fixed

$Y_{O_2} = 1.9213$ $BuCO_3 = 6.9770$ $CO = 3.8217$

$Y_{O_2} = 1.9213$

$BuCO_3 = 6.9770$

$CO = 3.8217$

2.1495
 0.2289
 1.9212

7.2050
 0.2297
 6.9753
 5.4214
 1.55

4.0499
 0.2281
 3.8218

4.0498

12.72

Some bumping, but very good mix as should be true. 12.35 post mix

12.72 of expected

REDO (Bumping too critical)

$Y_{O_2} = 1.9213$

$BuCO_3 = 6.9770$

$CO = 3.8217$

2.1425
 0.2240
 1.9215

7.1373
 0.2200
 6.9173

4.0425
 0.2210
 3.8215

4.0427
 $total$
 12.72

Mix recovery after sample drying: 12.63/12.72 $\Delta 0.7\%$ acceptable

~ 63.82
 $loss 51.19$

Post 62.35
 51.20
 11.19

Cal #I: 3:57 1900 w/5:15 est temp adjustment
4:25 486C \sim seems correct

(11.17 expected)
Post cal II

Post grad I: 11.21 \rightarrow 11.14 62.35

62.24
 51.20
 11.05

Very little lig formation compared to #2. Apparently need excess Bu and Co for large lig.

0.2 g loss due to Si contain from tube (pre-grad) 10.8

The above understood

Date

and

Date

4/27

10.97 collected: white top layer on powder. Dry, flake-like
very agglomerated/brittle and does not easily push out when
brushed. Had to dry grind in order to produce decent prod.
10.25 recovered after dry grind

P1 3500/29000

1.62	1.425	0.266	0.424	3.82	60—%
1.52	1.321	0.245	0.336	4.52	71 %

Pre-grind & Post-grind x-rays show change of some peaks
in two x-rays, however, scattering calculation of pellet may
return raw products to original ϕ 's. Will do x-ray of pellet
also.

Post: some slumping.

74 2/16/80 125 Duration Study IBM Technical Notebook Property Pellets
ave = 62.5

#1 P2 3.200/50,000
1.04 1.138 0.256 0.260 4 62.9
1.01 1.086 .22 0.189 5.34 84

#2 P2 1
1.02 1.0123 0.264 0.261(s) 9.90 67.3
REG 9.87 .22 0.188(s) 5.75 93.6

#3 P2 ✓
1.04 1.159 0.248 0.258 4.03 63.4
1.024 1.024 .224 0.184 5.54 87

Pellets N Process @ 10:30 A.M. 2/17/80 10°/min (prewarmed)
T_c T_s (3)
10:30 259 239
→ 10:45 442 518 +Δ 75-T_s
11:50 900:30 944

from early results, ΔT₀ too wet down
by 25°C estimated time to reach
at point would be 45 mins. or
11:30 @ +Δ 50 preheated
or 95°C then reequilibration over
existing 20 mins. of 60°C delay
in problem run - significant time
loss. B.C. is probably clear.
project over 2 hrs. 1:45 Mon.

1:45 PM 2/17/80 in furnace @ 600C

see page 147

2/6/89

Experiments to look at
Carbonate in 123

clean gas with oxygen

Sample 1. dense closed

porosity, $\approx 91\%$

cut sections from center

Sample 2. open porosity

$P.L. 9.2\%$

center sections

thin slices aggregate

(3) 3 pellets of each (Petio)
center sections of each

(1) T. am / FELSS (P. B. B. B.)

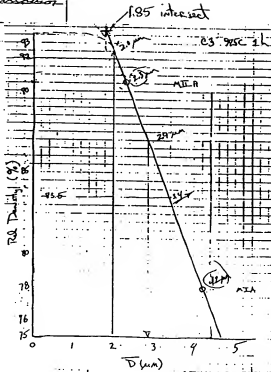
(2) Magnetometer (T. Magnet)

(3) Induction (D. B. B. B.)

(4) CO_2 evolution on dissolution

(5) X-ray diffraction

(6) XPS



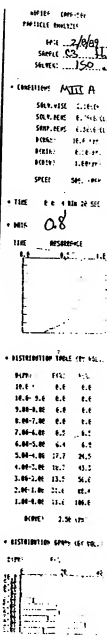
The above understood

Date

and

by

Date



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and witnessed by:

Date _____ and _____

Date _____

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2/7/89

PI mill D = 4.21 μ m (guide)

3353/28500

Pre wgt: 3.46 (of 3.5) some deformation during iso pressing, but slight
minimal so consistency can be checked.

Post 975C 1h

3.41 1.402 0.448 0.69 4.94 (77.7) \rightarrow 78% 4.2 too low

PII mill D = 2.34 μ m (slow)

Pre 3900/29,000

3.46 1.453 0.543 0.9 3.84 60.5 2, reasonable

3.40 1.285 0.456 0.59 5.76 90.6 <NEED SLIGHTLY HIGHER>

Tomorrow \rightarrow will mill in

the

Yields: Pre 50 MI: Post 48g

gap B

gap A { 24 MIIA: 20g
16 MIIIA: 4g

20.5

error in pre-weights

78 M4A $\bar{D} = 1.85$ Pre-IBM Technical Notebook

P3 (3.40) 1.452 543 0.9 3.78 20/mm to 675 10/mm to 975
1.288 1.265 0.460 0.578 6.02 94.6
3.48

P4 (3.41) 1.462 540 0.91 3.75 58
3.60 1.274 0.468 0.596 6.04 95
long

P5 (3.93) 1.457 0.561 0.925 3.67 57.7 $\rightarrow \geq 58$
3.60 1.280 0.482 0.62 5.81 91.4
3.65 5.89 92.6
{Probably even higher}

M4B - 4000/30,000 80 mm

P6 (3.53) 1.463 0.508 0.85 4.17 65.6
3.53 1.385 0.674 5.24 82.4 short

P7 (3.54) 1.462 0.504 0.85 4.165 63.5
3.59 1.358 0.462 0.68 5.36 84.5 long

P8 (3.56) 1.463 0.507 0.85 4.19 65.9
3.73 1.352 0.453 0.65 5.73 90.2

* laminated on 1 side, not severe (must be repelletized pellet)

6:15

P9 4000/30000

3.57 1.462 0.517 0.87 4.1 64.5

3.56 1.354 0.463 0.666 5.35 84.2

P10 fines 4/3.00 above

1.53 1.436 0.254 0.411 3.72 58.5 was expanded

1.54 1.254 0.207 0.256 6.02 94.7 } doesn't look good

Pellet cutting NEXT (see pg 80 for flow overview)

Pellet 3 & 4 dedicated to vertical & horiz slicing

Pellets 6 & 7 ↓ ↓ ↓ ↓ ↓

from tangent saw cut edge: 1 mm slices are 0.055" of blade

Low Density Vertical slices: 1 1.2 slices } 7 altogether + one piece
6 1.0 slices } and polished end (cylinder)

Horizontal: 2 1.0 slices mid section
1 0.5 top
1 1.0 bottom

High Density

vertical: 5 slices (and last to chipping) lead polished
~2 mm → 1 polished thick chunk
~1.2 mm } 3 oxygenated
1 SAE

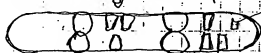
horiz: 2 mid section
1 ea top & bottom (top chipped)

IBM Technical Notebook

285/89

10/ Oxygenation Diagram { scheme

Top View



specimens 4.14d
on clean Al_2O_3 surface

LD marker (and place)

\leftarrow O_2 flow

2/14 IN AND to 6000 @ 200/min; 100/min to 8000

15 min SOAK AND start ramp to 6000 @ 0.17/min (10%/h)

To 600C @ 1:30 p.m. 2/15/89 in dry, CO_2 -free O_2 .

Relat (1) $0 \neq c$

1 mm vertical slices

⑤ 14 min to 850°C, 10 1/2 h to 600 °C
(48 h), quench.

- 1) ✓ slice for Jacoby Bros (Pamirco)
- 2) ✓ 1 slice for Alex for XPS of fracture surface
- 3) save remainder for future use (classified)
- 2A) 1 extra slice organized

Pellet (2) 0.1 C

inner horizontal slices 4 of outer slices discarded

- 1) 1 slice (80mm) goes to ASMR } at 8 mm index up
 otherwise for supernat del (if possible).
 1 disc to Tom
 2 discs in TEAM
 1 space
- 2) 1 slice dedicated to RT to Dave's specs

Pr. 11. (3) $\mathbb{D} \nsubseteq C$

space for (1) x-ray lattice
(2) CO₂ evolution

2/16/89

C4 Synthesis Preparation/Notes (last book IV, pg 46 of 14)

	oxide wt. fac.	atomic % 1/4 Ba C	oxide MW
V_2O_5	0.17(5)	.17	225.81
	51		
BaO	0.44(5)	.33	153.34

CO : 0.36(25) ~ .5 79.54

So with the new

Example Calc: wt. fac. deriv

$$V_2O_5 \quad 225.81 \text{ g} \times \frac{0.17}{100} = \frac{38.39}{2} = 19.19$$

$$19.19 / 109.36 = 0.1751$$

$$BaO \quad 153.34 \times .33 = 50.60$$

$$50.6 / 100 = 0.4618(5)$$

$$CO \quad 79.54 \times .5 = 39.77$$

$$39.77 / 109.56 = 0.363$$

$$0.9999$$

$$17.51 \text{ g } V_2O_5 \quad \nearrow 1.287009$$

$$46.18 \text{ g } BaO \left\{ \frac{197.35}{153.34} \times 46.18 \right\} = 59.43 \text{ g } BaCO_3$$

$$V_2O_5 \quad 19.19 / .99 = 19.209 \rightarrow 19.21 \quad \Rightarrow \times 1.5 \quad 28.81(5) \quad 28.82$$

$$BaCO_3 \quad 50.60(2) \times \left(\frac{197.35}{153.34} \right) = 65.12(5) \quad 97.69 \quad 97.69$$

$$CO \quad 39.77 / .99 = 39.87 \quad 59.71(5) \quad 59.72$$

$$97.69 (0.177) = 75.91 - 97.69 =$$

$$186.23$$

$$- 21.78$$

$$164.45$$

↑

A2

Administrative Notes

FINAL Batch Size for REASONABLE BULK HANDLING

$$\frac{1}{2}O_2 \quad 17.51/.999 = 17.52(7) \approx 17.53$$

$$BaCO_3 \quad 65.12(5)/.999 = 65.12(5) \approx 65.13 \quad \text{--- 343.78 ---}$$

$$C_2O \quad 39.77/.999 = 39.80(9) \approx 39.81$$

$$122.47$$

$$\begin{array}{l} 343.78(9) \quad BaCO_3 \quad \frac{1}{2}O_2 \quad 17.53' \text{ weighed/transformed} \\ \text{tare } 208.65 \\ \hline 65.13 \quad \checkmark \quad (A.O.01\%) \end{array}$$

$$\begin{array}{l} 382.46 \quad C_2O \quad \text{Mixing yield} \quad 122.29 \text{ g} \quad 99.85\% \\ \text{t } 343.78(7) \quad \hline 39.78 \quad (A.O.03\%) \quad \hline 122.47 \quad - A.O.15 \end{array}$$

$$\begin{array}{l} 151.42 \text{ OK} \quad 140.48 \text{ } \rightarrow \text{X bad batch dimensions} \\ \text{tare 1 } 32.89 \quad \text{tare 2 } 82.12 \\ \hline (68.93) \quad \hline 68.36 = 122.29 \quad \checkmark \end{array}$$

$$\begin{array}{l} 146.97(6) \\ 88.61 \\ \hline 58.36 \quad \swarrow \text{centered machine/some ice form} \\ \text{tare 1 } 151.42 \\ 144.37 \\ \hline 7.05 \\ 87.55 \end{array}$$

$$\begin{array}{l} 146.97 \quad \nwarrow \text{less centered, less ice} \\ 141.74 \\ \hline 52.23 \\ 88.61 \\ \hline 12.28 \text{ (2 lbs vs 14.53 expected)} \\ 105.6 \text{ (reacted)} \\ 2.25 \text{ to go} \end{array}$$

$$\begin{array}{l} \text{after gross } 108.71/110. = 98.8\% \quad - A.12\% \\ 197.983 \text{ (2)} \\ 88.64 \\ \hline 108.69 \end{array}$$

	Y	BaCO_3	CaO	SS / Result
C4-1	0.17	0.33	0.5	assumed stone pack
	0.16	0.36	0.5	analytical determination
C4-2	0.17	0.33	0.5	analytical <u>lig</u>
Δ	+0.01	-0.03	-	
C4-3	0.16	0.35	0.5	analytical
Δ	-0.01	+0.02	-	
Δ_{net}	-	-0.01	-	
-3E	0.165	0.35	0.5	
Δ	-0.005	+0.02	-	
Δ_{net}	+0.005	-0.01	-	
C4-4	0.16	0.34	0.5	analytical
Δ	-	-0.01	-	
Δ_{net}	-	-0.02	-	
C4-5	0.16	0.34	0.49	analytical
Δ	-	-	-0.01	
Δ_{net}	-	-0.02	-0.01	Species Imputation \rightarrow trace carbon,
C4-6	0.16	0.34	0.478	$\text{CaO} \rightarrow \text{Ca}_2\text{O}$
Δ	-	-	-0.02	$\text{BaCO}_3 \rightarrow \text{Ba(OH)}_2$
Δ_{net}	-	-0.02	-0.03	$\text{Y}_2\text{O}_3 \rightarrow \text{Y}_2\text{O}_3 \times$
C4-7	0.16	0.34	0.478	
Δ	-	-	+0.008	
Δ_{net}	-	-0.02	-0.022 \uparrow	

C4-7 TRANSFORM TO STOIC basis

Y_2O_3	BaCO_3	CuO	
0.17	0.31	0.478	0.48

Correct for final batch

% Y_2O_3 is good as received

BaCO_3 is Barium rich by 0.02 at %

CuO is Copper rich by 0.02 at %

A3

Administrative Notes

Post Cal II: r-bolts @ 950C in O_2

3/27

$$195.52 \rightarrow \text{post } 88.84 \text{ (22g rxn)}$$

$$88.64$$

$$106.88 - 108.69 = 181 / 2.25 = 80.5\% \text{ of remainder}$$

$$\frac{12.28}{14.09 / 14.53 \text{ there}} = 97\% \text{ }^{\dagger} \text{ loss}$$

Minimal loss formation

99.57g yield (due to contamination)

{ further contamination upon re-synthesis to the Pb catalyst reduces yield further

Peaks @ ~30.2, 19.4, 28.5 20 Linderberg. May be $PbCl_2$, but could also be Zr

$$n\lambda = 2d \sin \theta \Rightarrow \delta = \frac{\lambda}{2} \sin \theta \quad 100 = 3.72$$

scattering angle

$$3.72 = \frac{\lambda}{2} \sin \theta$$

$$4.883 = \sin \theta$$

4/19

From Hochstet: $1/96 Ba_{2.16} Cl_3$ ($1/32 Ba_{1.72} Cl_1$) $O_{2.2}$

In reference to variational study: $\frac{+0.01}{+0.005} \frac{0.36}{0.5} = 1.02$

975C "Property Pellet" information study - D₂

2 g. pellets should give enough material for 4.4 mm thick sintered body allowing a slice to be cut up an interior & exterior surface.

7.5 g #1 stock 192 used Son pellet (17.33.5)

2.6 g #2 stock 190 ↓ (15.33.52)

8.5 g #3 stock ✓ (17.35.48)

9 #4

2.7 #5 to 600C @ 20/min; 10/hw to 975C 4131-625C
3600/29,000 Over 1 h ~ 5110

#1 P3

192	1.144	0.479	0.489	3.93	61.8
190	1.0	0.4	0.314	6.05	95-

#2 P3

191	1.126	0.490	0.488	8.91	61.5
1.88(9)	0.98	0.412	0.311	6.05	95-

#3 P2

1.133	0.503	0.507	3.85	60.5	
1.95	0.998	0.43	0.336	5.57	86.6

1.85

#4 P2

1.139	0.481	0.490	3.88	61-	
1.90	1.05	0.43	0.37	5.05	79-

1.86

#5 P3

1.145	0.46	0.474	3.99	62.7
1.89	0.993	0.388	2.300	6.2

1.86

1.05

0.4

#1-5

P243 slicing of oxygenation @ 6000 for 66 hrs on D₂

0.394 inches

0.157 in for center cut

OPB ~ 2 mm



#1 P4 Pre 63.5%

Pot 1.85 1.025 0.406 0.335 5.52 87

2/28 Property Pellet Summary (to date)

	stin	lig	X	X	C.O	REA/TH	
	t	#1	#2	#3	#4	#5	
avg	975	(95)	95	(87)	(79)	975	R3
to surface 2/28	950 II	(84)	(99)	—	—	(87)	R2
	950	87	Rdane				R4
MICRO STRUCTURE	ORIG 950	91	'97'	71	78	92	Davis

 950th #1 & #5 pellets to temp @ 600C then 10C/mw Ramp @ 6:15 pm
 > oxygenation run
 Quit 10:00 A.M. 3/2 40h D₂

$$5 \text{ cc} \times \frac{6.36 \text{ g}}{\text{cc}} = 31.8 \text{ g}$$

$$\frac{\pi (2.54)^2}{4} X = 5 \text{ cc}$$

$$5.07 \text{ cm}^2 X = 5 \text{ cc}$$

$$X = 5 \text{ cc} / 5.07 \text{ cm}^2$$

$$X \approx 1 \text{ cm} \text{ or } 1/2 \text{ inch} - 1 \text{ inch with shrinkage}$$

4/24/89

#4 - C3 wt% Cu 28.7

wt% holes 36.0

Hole Concentration Conversion Formula:

Data: wt% Cu (total): 28.7

wt% holes: 36.0

$$\frac{\text{wt\% holes} - \text{wt\% Cu}_{\text{total}}}{\text{Cu}_{\text{total}}} = \frac{36 - 28.7}{28.7} = 0.254$$

average 'over'
balance

 $\therefore \text{add Cu balance (2)} = 2.25 \approx \text{average balance Cu}$

$$2.25 (\text{Cu}_{\text{total}}) = 2.25 (3) = 6.75 \text{ total Cu val}$$

$$+ 7.00 \text{ total Ba + Y val}$$

$$13.75$$

↓
total charge

Take total charge & divide by two for O^{2-}

$$13.75/2 = 6.88 \text{ O atoms} \Rightarrow YBa_2Cu_3O_{6.88}$$

see
page after
next

Notes to Kristy concerning Peter's ORANGE precalculations

To estimate pellet ^{pack} weight for pellet pressing:

1. take dia dia & approx. height desired
1. calculate volume in cc. (ie. $\frac{1.22^2 \times 0.35 \times \pi}{4} = 0.41 \text{ cc}$)
2. Assume some reasonable 'green' density (which varies pellet)
0.6-0.8 (60-80%) usual for metals > 0.70 up small
ave. part. dens. (ie. 3.14).

$$\left(\frac{0.41 \text{ cc}}{0.8} \right) \times 90 \frac{\text{g}}{\text{cc}} \approx 35 \text{ g of powder}$$

(density theoretical)

I pressed @ between 16,000 & 29,000 psi.

low side for pure metal \therefore

$$\frac{x}{(\text{dia})^2} = \text{desired pressure} \quad \text{where } x = \text{1" dia. pressure}$$

$$x \approx 4000 \text{ for } 0.48" \text{ dia. die.}$$

ANALYST: JPY-SM
 PARTICLE ANALYZER:
 MET: 3/1/89
 SAMPLE: 2550-6
 SOLVENT: 150

MODELING: CUPR-500
 PARTICLE ANALYZER:
 DATE: 3/1/89
 SAMPLE: 2550-6
 SOLVENT: 150

* CONDITIONS:
 SOLV. VISC: 2.10 CP
 SOLV. DENS: 0.791 G/CC
 SHAP. BECS: 3.976 G/CC
 WINDUP: 18.8 CPM
 ROTARY: 1.000 CPM
 SPEED: 500.0 RPM

* CONDITIONS:
 SOLV. VISC: 2.10 CP
 SOLV. DENS: 0.791 G/CC
 SHAP. BECS: 3.976 G/CC
 WINDUP: 18.8 CPM
 ROTARY: 1.000 CPM
 SPEED: 500.0 RPM

W. 15.000 22.000

* JIM: 10.0 2.0 10.0 30.0

* MIN-D = 0.9

RESPONSE

RESPONSE

* DISTRIBUTION TABLE (CP VOL.)

WINDUP	CPM	CPM
10.0	0.5	0.5
10.0-5.0	2.0	11.2
5.0-4.0	3.0	15.2
4.0-3.0	7.0	22.4
3.0-2.0	7.4	29.6
2.0-1.0	17.6	47.2
1.0-0.5	27.2	64.2
0.5-0.0	31.2	76.4
0.0-0.0	33.4	82.6
0.0-0.0	34.4	90.8
0.0-0.0	35.2	100.0

* DISTRIBUTION TABLE (CP VOL.)

WINDUP	CPM	CPM
10.0	0.4	0.4
10.0-5.0	4.5	4.5
5.0-4.0	0.4	4.5
4.0-3.0	0.4	4.5
3.0-2.0	0.4	4.5
2.0-1.0	0.4	4.5
1.0-0.5	0.4	4.5
0.5-0.0	0.4	4.5
0.0-0.0	0.4	4.5
0.0-0.0	0.4	4.5
0.0-0.0	0.4	4.5

* DISTRIBUTION GRAPH (CP VOL.)



* DISTRIBUTION GRAPH (CP VOL.)



Analytical Results for CS H₂/LD STUDY - Hole

IBM

IBM
RESEARCH CENTERANALYTICAL
LABORATORY

Request for Analysis

Use Ball Point Pen

QUESTION <u>1.5 Holes</u>	PROJECT NO. <u>25-232</u>	DETECT NO.
DEPARTMENT	LOCATION	PHONE
REQUESTOR'S SAMPLE IDENTIFICATION <u>Hole 1, LD</u>		
APPROXIMATE COMPOSITION AND HISTORY OF SAMPLE <u>Y₂O₃ Cu Oxide</u>		
ANALYSES REQUESTED		
ANALYSIS METHOD		
(Cont)		
ANALYTICAL RESULTS		
<u>6.7% H₂O</u>	<u>H₂O</u>	<u>LD</u>
	<u>33.5</u>	<u>34.2</u>
<u>→ 10.9% Cu</u>	<u>(27.5)</u>	<u>27.6</u>
	<u>2.21</u>	<u>2.21</u>
	<u>681</u>	<u>9.689</u>
<u>tot. H₂O = 7%</u>		
<u>Fe</u>		
<u>Aster. Reox. 11 Dax</u>	<u>28.7</u>	<u>17.6</u>
<u>pure Cu spec</u>	<u>36</u>	<u>6.8</u>
DATE SUBMITTED <u>5/11/67</u>	DATE REPORTED <u>5/14/67</u>	WORKBOOK REFERENCE <u>4/11/67 p. 121</u>
ANALYST <u>J. L. Smith</u>	APPROVED	

Nº

Notes to Kristy concerning Forming precalculations

To estimate pellet weight for pellet pressing:

- A. take dia dia & approx. height desired
 1. calculate volume in cc. $(\frac{1}{2} \pi \text{dia}^2 \times \text{height}) = 0.41 \text{cc}$
- B. Assume some reasonable 'green' density (wt% of pellet)
 - 0.6-0.8 (60-80%) usual. For metals > 0.70 or so
 - ex. pot. dia. (ie. 3mm)
 - C. density theoretical

$$\frac{0.41 \text{cc}}{0.8} \times 90 \frac{\text{g}}{\text{cc}} \approx 3 \text{g of powder}$$

I pressed @ between 16,000 & 29,000 psi.

low side for pure metal.

$$\frac{X}{(\text{dia})^2} = \text{desired pressure where } X = 1'' \text{ scale pressure}$$

$$X \approx 4,000 \text{ for } 0.48'' \text{ dia. dia.}$$

4/24/89

#1-C3 wt% Cu 28.7

wt% holes 36.0

Hole Concentration Conversion formula:

Data: wt% Cu (total): 28.7

wt% holes: 36.0

see
page after
next

$$\frac{\text{wt\% holes} - \text{wt\% Cu}}{\text{Cu wt}} = \frac{36 - 28.7}{28.7} = 0.254 \quad \text{average iron valence}$$

∴ add Cu valence (2) = 2.25 = average valence Cu

$$2.25 (\text{Cu wt}) = 2.25 (3) = 6.75 \quad \text{total Cu val}$$

$$\begin{array}{r} \text{Sum charges} \\ \text{y. Ba}_2\text{Cu}_3 \end{array} \quad \begin{array}{r} + 7.00 \quad \text{total Ba + Y val} \\ \hline 13.75 \end{array}$$

total charges

Take total charges / divide by two for O²⁻

$$13.75 / 2 = 6.88 \text{ O atoms} \Rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6.88}$$

Notes to Kristy concerning Pellet Forming precalculations

To estimate pellet weight for pellet pressing:

1. take d_1 & d_2 & approx. height desired
 & calculate volume in cc. $(\frac{\pi d^2}{4} \times \text{height}) = 0.41 \text{ cc}$

2. Assume some reasonable 'green' density (carbon pressed pellet)
 0.6-0.8 (60-80%) usual for metals > 0.70 if small
 ave. part. diam. (i.e. 3 μm).

$$(0.41 \text{ cc} / 0.8) \times 9.0 \text{ g/cc} \approx 3 \text{ g of powder}$$

I pressed @ between 16,000 & 20,000 psi.

low side for pure metal.

$$\frac{X}{(\text{inch})^2} = \text{desired pressure where } X = 1'' \text{ side pressure}$$

$$X \approx 4000 \text{ lbs for } 0.48'' \text{ dia. die.}$$

Analytical Results for C3 HV/LD STUDY - Holes

IBM

IBM
RESEARCH CENTER

ANALYTICAL
LABORATORY

Request for Analysis

Use Ball Point Pen

ANALYST <u>J. S. Hines</u>	PROJECT NO.	REQUEST NO.
DEPARTMENT	LOCATION	ROOM <u>25-235</u>
REQUESTOR'S SAMPLE IDENTIFICATION <u>Holes, L.Dex</u>		PHONE
APPROXIMATE COMPOSITION AND HISTORY OF SAMPLE <u>Y₂O₃ Co Oxide</u>		
ANALYSES REQUESTED		
ANALYSIS METHOD <u>Chem</u>		
ANALYTICAL RESULTS		
	H ₂ O	LD
<u>45% H₂O</u>	<u>33.5</u>	<u>34.2</u>
<u>71.6% Co</u>	<u>(27.5)</u>	<u>(27.6)</u>
<u>2.21</u>		<u>2.21</u>
<u>681</u>		<u>4.69</u>
$\frac{\text{Total} = 7\%}{4\%}$		
<u>After Recox: H₂O</u> <u>pure 62.50%</u>	<u>28.7</u> <u>36</u>	<u>71.6%</u> <u>holes</u>
		<u>2.21</u>
DATE LABORED <u>5/17/87</u>	DATE REPORTED <u>5/24/87</u>	ANALYST'S SIGNATURE <u>J. S. Hines</u>
ANALYST	APPROVAL	REFERENCE <u>Y/11/24/87</u>

No.

Recalculating Pre HD, LD values w/ 28.7% C

$$\text{HD takes } 33.5 \therefore \frac{33.5 - 28.7}{28.7} = 0.167$$

$$2 + 0.167 = 2.167 (3) = +6.50$$

$$+ 7 =$$

$$13.50 / 2 = 6.75 \Rightarrow \gamma \text{Ba}_2\text{Cu}_3 \text{ } ^{2447} 0.675$$

$$\text{LD } \frac{34.2 - 28.7}{28.7} = 0.192 \quad 2.192 (3) = 6.58$$

$$+ 7$$

$$13.58 / 2 = 6.79$$

$$\therefore \gamma \text{Ba}_2\text{Cu}_3 \text{ } ^{2.192} 0.679$$

with original mod. C values

$$\text{HD } \frac{33.5 - 27.5}{27.5} = 0.22 \quad 2.22 (3) = 6.66 + 7 = 13.66 / 2 = 6.83$$

$$7$$

$$\text{LD } \frac{34.2 - 27.0}{27} = 0.27 \quad 2.27 (3) = 6.81 + 7 = 13.81 / 2 = 6.90 (5)$$

$$\text{w/ ave } 27.5 + 27 = 27.25$$

$$\text{LD } \frac{34.2 - 27.25}{27.25} = 0.25 (5) \quad 2.255 (3) = 6.765 = 13.765 / 2 = 6.88$$

$$\text{HD } \frac{33.5 - 27.25}{27.25} = 0.23 \quad 2.23 (3) = 6.69 \text{ } ^{6.845} \text{ } ^{6.845} \text{ } ^{6.845}$$

Composition ##	Rel Pellet [*] density (%)	Actual Density	Green Rel δ	Green act δ
1	84 (90.8)	5.34	62.8	4.0
2	96.8	5.95	61.5	3.90
3	71	4.52	60-	3.82
4	77.8	4.95	62	3.93
5	87 (91)	5.54	63.9	4.03

* after 1h sinter @ 950C